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PREFACE

At present the field of intermolecular interactions, or to use the current phrase 'molecular interactions', is one of the major areas of molecular science. One reason for this is that the topic is important in chemistry, physics, and biology, and even more so at the interfaces of these subjects.

The present and the next issues of the *Proceedings* discuss a variety of important aspects of the subject. They contain important topics which have not recently been dealt with in an authoritative fashion, such as the information given by studying hindered internal rotation. This group also includes treatments of the liquid crystalline, plastic and glassy states which are to some extent, complementary. They also contain contributions based largely on nuclear magnetic resonance work. Nuclear spin relaxation studies have led to intimate knowledge concerning association effects. The approach developed principally at the Karlsruhe Laboratory is described. Also included is a second experimental chapter devoted to the way in which light scattering studies provide information on multipole forces in molecular interactions. Other topics based on NMR studies show how this technique yields valuable information on molecular and ion-molecule interactions respectively.

It is a pleasure to thank all authors who have contributed to these special issues.

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Hindered internal rotation and intermolecular interactions

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1. Introduction

Flexibility of chemical bonds is one of the important factors that determine the properties and reactivity of a molecule. Most chemical bonds, while not completely rigid, still are not involved in totally free rotation. With the development of various physical methods of investigation, it has become evident that the internal rotation about a bond is hindered to varying degrees. The earlier investigations of internal rotation mainly used the methods of dipole moments and Raman and infrared spectroscopy, and the results are summarized in an excellent monograph written by Mizushima (1954).

Hindered internal rotation at ambient temperatures was first detected by means of nuclear magnetic resonance (NMR) in N,N-dimethylformamide (DMF) in the middle of the nineteen-fifties by Phillips (1955) and Gutowsky and Holm (1956). It was observed that the bandshape of the NMR spectrum of DMF was modified, depending on the rate at which the two methyl groups exchanged sites. The resulting bandshapes were then analysed based on the modified Bloch equations (Gutowsky and Saika 1953; Gutowsky and Holm 1956) to yield the rate of the exchange. Subsequent to these original works, a large number of bandshape studies have been reported on amides. The special attention given to this class of compounds may be attributed partly to the fact that the dynamic process for the carbon-nitrogen bonds in amides as detected by NMR usually takes place at an easily accessible temperature range (the barrier to rotation being around 50 to 90 kJ/mol), and also partly to the importance of the amide linkage in peptides and proteins.

Determination of smaller energy barriers has been made possible by improvement in the variable temperature equipment, by the use of nuclei other than protons, and/or by the introduction of higher magnetic field strengths and pulse and FT methods. At the same time, the bandshape calculation has become much more precise for coupled spin systems with the introduction of a quantum mechanical approach using the density matrix procedure (Kaplan 1958a, b; Alexander 1962a, b).

Complete bandshape analysis has now been well established and comprises the principal method of the branch of NMR called dynamic nuclear magnetic resonance (DNMR). Other methods include the use of relaxation times and the double resonance technique, which are especially valuable in obtaining information about those dynamic properties of the system which occur at rates too fast or too slow for the application of bandshape methods, even though the interpretation of the data is rather complex. A

In many of these studies, the observed thermodynamic data are explained in terms of the effects of substituents and steric hindrance on internal rotation, as well as the effect of molecular interactions. Compared with the former two effects, the effect of molecular interactions on internal rotation has not been well understood, due partly to the small size of the effect and also to the complexity of the interpretation which has to take into account the microscopic environment of the rotational isomers in solutions. Nevertheless, a few measurements in the gaseous state as well as theoretical calculations using molecular orbital or force field methods have indicated that a significant difference may exist in the barriers to internal rotation in liquid state as compared to gas. In view of the fact that most of the measurements are made in solutions, it is essential to obtain a much greater knowledge of the effect of solvation and molecular associations on the rate of hindered internal rotations.

Excellent reviews are available on DNMR studies of internal rotations: Binsch (1968), Kessler (1970), Stewart and Siddall (1970), and Sutherland (1971) dealt thoroughly with the studies up until 1969 in their reviews. 'Internal Rotation in Molecules' edited by Orville-Thomas (1974) discusses the studies made by various physical methods including DNMR. Further, in 1975, Jackman and Cotton (1975) edited an extensive review book, 'Dynamic Nuclear Magnetic Resonance Spectroscopy', which describes in detail the theories, methods and application of DNMR and contains all the main studies reported up to 1974.

Thus this article will present selected examples of more recent studies on hindered internal rotation which appeared mainly from 1974 to 1983. Since the attention is to be focussed on the effect of molecular interactions, it will not be an exhaustive article covering all the main studies. Examples chosen will also be dependent on personal interest and availability. Results reported in literature on the carefully determined values of activation enthalpies ($\Delta H^\ddagger$) and entropies ($\Delta S^\ddagger$) have been included to the greatest extent possible despite the reputed uncertainty in these parameters as compared with free energy of activation ($\Delta G^\ddagger$) values, though, unfortunately, a large number of studies list $\Delta G^\ddagger$ values only. Due to limited space, no works on metal compounds are included, neither are the DNMR works on ring reversals or nitrogen inversion except for a few examples. SI units are used throughout the text; the conversion factor of 4.184 J/cal has been applied to the published thermodynamic data where necessary.

2. Methods of measurement

Since excellent treatises have been published recently on practical aspects of DNMR (Binsch 1975; Kaplan and Fraenkel 1980; Sandström 1982), only a few points will be selected and discussed here.

2.1 Complete bandshape analysis

The method of calculating nuclear magnetic resonance bandshapes in the presence of chemical exchange processes was first presented by Gutowsky *et al* (1953) as a direct modification of the Bloch equations to incorporate the effect of exchange. This 'classical' bandshape method for the uncoupled two-site exchange model and its various extensions such as to *N*-site models and weakly coupled systems have been

molecular and intermolecular exchange processes. Various approximate procedures have been devised for slow, intermediate and fast exchange cases so that the rates may be obtained readily based on a single-parameter taken from the observed spectrum. Despite large errors often involved in these single-parameter approximations (Allerhand *et al* 1966; Kost *et al* 1971; Berg *et al* 1977), they have been quite frequently used.

Since the Bloch equations are derived for an ensemble of independent spins, the modified Bloch equations are also only applicable to uncoupled spin systems. Strongly coupled systems require a full quantum mechanical treatment in terms of a density matrix. Such a density-matrix method of bandshape calculations has also been well established and presented in forms suitable for computer calculations. See, for example, Binsch (1975) for a list of computer programs. Recent additions to the list include DNMR 3-IT2 (Musso *et al* 1978) and DNMR 5 (Stephenson and Binsch 1978) which incorporate least square iterative simulations.

Now that the theory and method of the complete bandshape calculation have been established and also efficient digital computers have become readily available for the calculations, this method is performed almost routinely in many laboratories. This is a welcome situation for the study of molecular interactions in this field, because the interaction energy is rather small compared to the energy barriers for internal rotations, sometimes within the margin of error limit of measurements, and thus the results may be significantly influenced by the accuracy of measurements. Furthermore, it has also been pointed out that such thermodynamic parameters as $\Delta H^\ddagger$ and $\Delta S^\ddagger$, which are notoriously susceptible to systematic errors, contain relatively more information concerning molecular interactions, as compared to relatively error-free $\Delta G^\ddagger$, the free energy of activation. Accordingly, accurate measurements are required to study the effect of molecular interactions.

Application of the bandshape analysis to obtain activation parameters involves; (a) obtaining mechanically undistorted spectral lines at a wide range of accurately measured temperatures, (b) simulating the obtained bandshape by calculating the theoretical line for the correct spin system and using accurately determined input parameters such as the population p , the spin-spin relaxation times T_2 , and the relative chemical shifts in the absence of exchange $\Delta\nu$, for the nuclei at each site, and (c) determining thermodynamic parameters from the temperature dependence of the statistically weighted rate data through Arrhenius' and Eyring's equations. This procedure, when carefully followed, is considered to give the most accurate rate constants and activation parameters for molecular rotations at present. Probable errors and means to minimize them in each of these steps are discussed in the reviews by Binsch (1968, 1975) and Szymanski *et al* (1977) and also in numerous articles, so only a few points will be mentioned here.

Narrow temperature ranges of study and uncertainty in temperature measurement are often listed as the primary sources of errors in bandshape studies. The conventional methods for measuring the sample temperature include inserting in the sample-holding space, (a) a thermocouple or thermister, or (b) an 'NMR thermometer' such as a tube or capillary containing methanol or ethylene glycol, under identical conditions to those used for the spectral measurement, and recording the emf or the chemical shift, both immediately before and after the bandshape measurement at each temperature. In the case of (b), the chemical shift of the strongly temperature dependent signals of these

minimize the temperature gradient along the sample tube and avoid refluxing of the solution inside the tube, especially when it is vacuum-sealed.

A source of error which is often overlooked or not correctly accounted for is the inherent temperature dependence of the bandshape parameters such as $\Delta\nu$, p and T_2 . This phenomenon is particularly marked in those systems where molecular association is considered to be significant. Usually, a linear dependence of these parameters on temperature is assumed, and the kinetically unaffected part of the linear plots is extrapolated to the coalescence region to obtain the necessary values. Nonlinear dependence has also been observed (Hólik and Mannschreck 1979).

Neglect of small long-range spin-spin couplings has been cited as a potentially important source of systematic errors in the bandshape analysis. The effect could be particularly evident on the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ (Drakenberg and Carter 1975). When dimethylacetamide was treated as an $A \rightleftharpoons B$ exchange system instead of $AX_3 \rightleftharpoons BX_3$ system which explicitly includes the five-bond long-range proton-proton coupling, the above authors showed that $\Delta H^\ddagger$ was different by about 10%, while $\Delta S^\ddagger$ was six times too large, demonstrating that a spurious 'entropy effect' can easily arise from neglect of unresolved long range couplings.

The accuracy of the measurement may be improved by deliberately selecting complex spin systems (Höfner *et al* 1978a, b). Similarly, the bandshapes of different groups or of multiple types of nuclei within a molecule may be studied to provide cross-checks on the result of a single rate process. If relaxation time measurement is conducted in conjunction with the bandshape study, a much wider temperature range may be studied to increase the accuracy (Bovéé 1979).

^{13}C DNMR with broadband proton decoupling has been gaining popularity recently, because of the very simple non-spin coupled spectra (which may be easily analysed by means of modified Bloch equations) and also because of the large chemical shift difference between the exchanging carbon signals. The large chemical shift difference between the exchanging carbons offers a wider temperature range to study especially when used in conjunction with ^1H DNMR, as well as allowing the measurement of lower barriers (fast rate processes). ^{13}C DNMR studies have been reviewed by Mann (1977b).

Large chemical shift differences are also commonly observed in ^{19}F spectra, but strong couplings between the fluorine atoms or with protons often give rise to more complex spectra. Such complexity has been utilized for added accuracy (Jost *et al* 1979). The prospect of and the problems involved in ^{15}N DNMR have been discussed by Roberts (1979).

^1H DNMR has been investigated in liquid crystalline samples (Schmiedel *et al* 1980) and in samples oriented in nematic solvents (Khetrapal and Kunwar 1982).

2.2 Other methods

2.2a. *Methods of relaxation times:* While complete bandshape analysis has been established as a standard tool for the investigation of internal rotation of molecules, its application is generally limited to processes with rates of 10^0 – 10^5 sec^{-1} . Important intramolecular motions such as methyl rotation and segmental motions along chain-

like molecules occur at a much faster rate, which may be studied by NMR techniques in terms of other important parameters, relaxation times. The range of measurable rates will then be extended in both directions to 10^{-2} – 10^{11} sec $^{-1}$. The theory and practical methods of application to exchange problems are discussed by Reeves (1975), Freeman and Hill (1975), and Sandström (1982).

Various techniques for the measurement of T_1 , the spin-lattice relaxation time, have been described and their accuracy compared by Weiss and his coworkers (Weiss *et al* 1980; Becker *et al* 1980). The spin-lattice relaxation time of nuclei may be represented by the expression,

$$1/T_1 = 1/T_{DD} + 1/T_{SR} + 1/T_Q + 1/T_{\text{other}},$$

where T_{DD} is the dipole-dipole contribution to the relaxation, T_{SR} the spin-rotation contribution, T_Q the contribution due to quadrupolar effect, and $1/T_{\text{other}}$ the contribution from all other types of relaxation. The relative importance of these contributions depends on the nuclei and the molecular system to be studied. The most important relaxation mechanisms for nuclei of spin = 1/2 in the liquid phase are intra- and inter-molecular dipole-dipole (DD) interaction and spin-rotation (SR) contribution, while for those nuclei with spins ≥ 1 a quadrupolar (Q) contribution is the predominant mechanism of relaxation.

In order to apply the available theory of relaxation and so obtain the desired information about the exchange processes from the experimental relaxation data, it is necessary to separate the data into each contributing mechanism. For protons, this is not easy in many cases because inter- and intramolecular dipole-dipole and the spin-rotation contributions are of comparable sizes and not easily separable. In favourable cases of small molecules, the separation has been accomplished by making full use of information obtained from the relaxation measurements of other nuclei in the same molecule (Suchanski and Canepa 1979). For larger and more complex molecules, measurement of multi-selective proton spin-lattice relaxation rates has been proposed as a useful technique in studies of the internal motions (Nicolai and Tiezzi 1979; Nicolai *et al* 1980).

On the other hand, the case of ^{13}C atoms directly bonded to protons has the advantage that the DD interaction is dominated by the carbon-proton dipolar interaction only (Kuhlman *et al* 1970), the amount of which can be estimated by observing the carbon-proton nuclear Overhauser enhancement (NOE) effect. The dipolar contribution to T_1 may thus be calculated and separated from the spin-rotation contribution. The obtained T_{DD} to which the intermolecular contribution is usually negligible is then interpreted to extract exchange rate according to the method developed by Woessner (1961, 1962), Woessner *et al* (1969). This treatment is particularly suited for the study of methyl group rotation. The temperature dependence of T_{DD} will then provide the thermodynamic activation parameters (Erickson *et al* 1980).

The spin-rotation relaxation time, T_{SR} , has also been found to yield the barrier to methyl group rotation. The contribution of T_{SR} has been obtained from the $^{13}\text{C}T_1$ and the NOE factors and related to the potential barrier of a methyl group (Zens and Ellis 1975; Tancredo *et al* 1978).

Information on the exchange rates may be obtained from the spin-spin relaxation

the spin-echo technique of Hahn or the Carr-Purcell (-Meiboom-Gill) pulse sequence is a function of the relative chemical shift $\Delta\nu_{AB}$, the lifetime τ_A and τ_B , and the transverse relaxation times at each exchange site, T_2^A and T_2^B (Luz and Meiboom 1963). The theory and the method have been described by Freeman and Hill (1975) and by Jen (1978), though not many applications have been reported.

2.2b. Saturation transfer: The application of double resonance for the study of chemical exchange rates was first proposed by Forsén and Hoffman (1963, 1964) and is called the saturation transfer method. In the case of a two-site exchange, for example, the size of the signal at one site is measured in the absence and the presence of a strong rf field at the second site, and the resulting intensity perturbations at the first site are studied. This method is applicable to slow exchange processes where the rates are of the order of 10^{-2} to 10^{-1} sec^{-1} and, if used together with bandshape analysis, may provide a powerful method of determining accurate activation parameters (Mann 1977a).

2.2c. Relaxation time coalescence: Another method which may be used to obtain information about the exchange rate in the slow motional range has been proposed by Lambert and Keepers (1980). They made a detailed analysis of the temperature dependence of non-selective ^{13}C spin-lattice relaxation times (T_1^A and T_1^B) for the N-methyl carbons, A and B, of N,N-dimethylformamide (DMF) and found the observed T_1^A to show a peculiar sigmoidal behaviour as the temperature is changed. This was explained as being due to a superposition of exchange effects on dipole-dipole relaxation. Regression analysis using a double-exponential expression yielded the rotational rate ($k = 1/\tau$) about the amide bond and the true relaxation times. The method is especially suitable for studies on exchange processes with high barriers since the effects of exchange on relaxation times were most marked at a temperature range below that where any lineshape change occurred.

2.2d. Equilibration method: When the exchange process is between non-identical isomers, rate of return to the equilibrium from a non-equilibrium condition will provide the rate constant for the exchange. This method is especially useful when a relatively large energy difference between the ground states of the isomers causes the population of the high-energy species to be too small to be studied by the bandshape method.

The system may be put into an initial non-equilibrium state by a number of means; a pure isomer may be produced by synthesis (Mannschreck *et al* 1967) or one of the isomers may be preferentially complexed and concentrated (Gutowsky *et al* 1967) at a temperature where the exchange rate is small enough. The NMR spectra are then studied as the mixture is brought to an equilibrium at a higher temperature. Anet and Squillacote (1975) demonstrated that a relatively high concentration of the minority form of N-methylformamide (*cis*) present at a high temperature (813 K) could be frozen out by depositing the mixture instantaneously to a surface of a very low temperature (208 K) to trap the high-temperature equilibrium ratio, and the rate was studied through the change in the peak intensities as the mixture was brought to equilibrium at the low temperature.

2.2e. Two-dimensional (2D) DNMR: The application of two-dimensional ^{13}C DNMR for chemically exchanging systems has been proposed by Ernst and his coworkers (Jeener

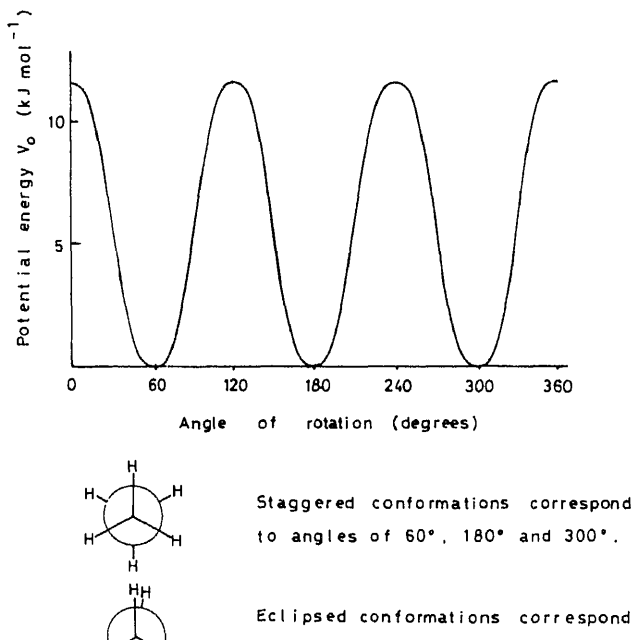
3. Hindered internal rotation about various bonds

3.1 Carbon-carbon bond

3.1a. *Substituted ethanes* (sp^3-sp^3): The barriers hindering internal rotation around single bonds in molecules are normally small. In ethane, the simplest molecule for which rotation around a carbon (sp^3)-carbon (sp^3) single bond is possible, the barrier to rotation is known to be of the order of 12 kJ mol^{-1} (Weiss and Leroi 1968). The potential energy of the molecule varies with the angle of rotation as shown in figure 1. The barrier to internal rotation measures the difference in energy between the staggered ground state and eclipsed transition state.

The origin of the barrier to internal rotation in ethane has been the subject of many theoretical discussions. Quantum mechanical calculations have shown that the main part of this barrier is caused by the orthogonality of the molecular orbitals that is required by the Pauli principle (Christiansen and Palke 1977; Morokuma and Umeyama 1977). Contributions from bond-antibond interactions have also been suggested as a possible primary contribution to the barriers from the result of an INDO calculation (Brunck and Weinhold 1979). When the two methyl groups are separated by three bonds, as in 2-butyne, $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$, the barrier to rotation becomes negligibly small, almost a thousand-fold; a microwave determination gives a barrier of less than 12 J mol^{-1} for the closely related molecule, methylsilylacetylene (Kirchoff and Lide 1965), and an *ab initio* calculation estimates it to be $20-25 \text{ J mol}^{-1}$ (Radom and Pople 1970).

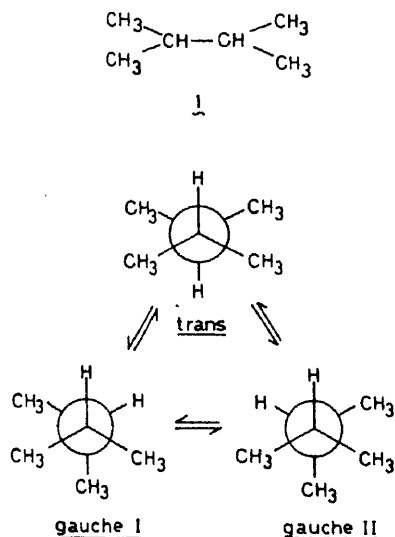
In addition to this intrinsic barrier found in ethane, contributions from steric and electrostatic attractive and repulsive interactions become important in determining the



various groups. This subject has been studied extensively by NMR and other techniques, and the experimental and theoretical results obtained before 1974 are included in a number of reviews (Binsch 1968; Kessler 1970; Sutherland 1971; Abraham and Bretschneider 1974; Sternhell 1975). It is only recently, however, that application of complete bandshape analysis became popular in the DNMR study of substituted ethanes. The extremely low temperatures required to slow down the rotation about single bonds with small barriers, as well as frequent isochrony of the chemical shifts of exchanging protons have been the main difficulties. Table 1 lists the barriers to C—C bond rotation that have recently been measured in substituted ethanes.

It has generally been observed earlier (Sternhell 1975) that in halogenated ethanes the barriers are dependent on the steric bulk of halogens, as well as the total number of the halogen atoms. In the case of alkyl substituents, an increase in the barrier with the group size is also evident, indicating that steric repulsions and electrostatic repulsive forces between the bonds of similar polarity are the important factors determining the barrier heights (Anderson *et al* 1976).

When there are two possible pathways for rotation with different barrier heights, the process with the lower energy barrier is found to take place exclusively. Lunazzi *et al* (1977a) employed 90.5 MHz ^{13}C NMR to study the *trans-gauche* interconversion in 2,3-dimethylbutane **1**. The two pathways are the *gauche-trans-gauche* process and the



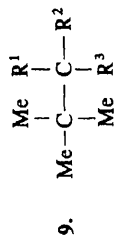
trans-gauche-gauche process. In a *gauche-trans* transition state, only one pair of methyl groups is eclipsed at a time, while in a *gauche-gauche* transition state, two pairs become eclipsed simultaneously. From the low temperature (173–93 K) bandshape analysis of the methine signal, together with an *ab initio* SCF-MO calculation, they concluded that the interconversion takes place exclusively via the *gauche-trans-gauche* process, with a free energy of activation of 18 kJ mol^{-1} . The calculation predicted that the *gauche-gauche* barrier would be about 33.5 kJ mol^{-1} .

Table 1. Barriers to internal rotation in substituted ethanes and propanes^a.

No. Compound	Substituent	Solvent ^c	T (K) ^b	$\Delta G_T^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
1.	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 \\ & \\ \text{CH}_3 & \text{CH}_3 \end{array}$	CHF ₂ Cl/ CH ₂ FCl	93	18.0			1
2.	$\begin{array}{c} \text{Bu}^t & & \text{Bu}^t \\ & \diagdown & / \\ & \text{CH} - \text{CH} \\ & / & \diagdown \\ \text{Bu}^t & & \text{Bu}^t \end{array}$	HCB/ DMSO-d ₆	413	96		2	
3.	$\begin{array}{c} \text{CH}_3 & \text{CH}_3 \\ & \\ \text{Bu}^t\text{CH}_2 - \text{C} - \text{C} - \text{CH}_2\text{Bu}^t \\ & \\ \text{CH}_3 & \text{CH}_3 \end{array}$	CHF ₂ Cl	254.5	57.7			3
4.	$\begin{array}{c} \text{Me} & \text{X} \\ & \\ \text{Me} - \text{C} - \text{C} - \text{C} - \text{Me} \\ & & \\ & \text{Me} & \text{Me} \end{array}$	CHFCl ₂ CH ₂ Cl ₂ CHFCl ₂ CHFCl ₂ CH ₂ Cl ₂ CF ₂ Cl ₂ CF ₂ Cl ₂ CF ₂ Cl ₂	143.4 149.8 216.6 214.2 206.9 170.0 154.5 152.1	29.2 33.6 43.6 44.9 46.6 36.4 32.6 32.6	41.4 37.2 43.4 49.9 16.7	51.0 -29.7 -2.1 16.7	3 4 3 3 3 5 5 5

Table 1. (Continued)

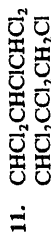
No. Compound	Substituent	Solvent ^c	T (K) ^b	$\Delta G_f^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
5.	$\begin{array}{c} \text{Me} \quad \text{X} \\ \quad \\ \text{---C---C---Me} \\ \quad \\ \text{Me} \quad \text{Cl} \end{array}$	CHCl ₂	205.2	44.7	46.0	7.5	3
	X = CH ₂ Ph	CHCl ₂	209.0	45.4	39.9	-25.9	3
	X = CH ₂ Bu ^t	CHCl ₂	220.1	49.4			3
	X = Bu ^t	CHCl ₂	212.9	47.8	49.5	8.8	3
6.	$\begin{array}{c} \text{Me} \quad \text{X} \\ \quad \\ \text{Me---C---C---Me} \\ \quad \\ \text{Me} \quad \text{CH}_2\text{Ph} \end{array}$	CHCl ₂	151.2	29.7	29.5	1.7	3
	X = Br	CHCl ₂	212.0	47.3	36.7	24.7	3
7.	$\begin{array}{c} \text{OR} \quad \text{X} \\ \quad \\ \text{Me---C---C---Me} \\ \quad \\ \text{Me} \quad \text{Me} \end{array}$	<u>OR</u>	193	41.8	36.4	-26.4	6
		Me	193	41.0	36.0	-24.7	6
		Et	193	41.8	33.9	-41.4	6
		Et	193	41.0	33.1	-41.8	6
		COMe	193	41.8	36.4	-26.8	6
		COMe	193	40.6	32.6	-41.8	6
		<u>X</u>					
		Br					
8.	$\begin{array}{c} \text{OR} \quad \text{X} \\ \quad \\ \text{Me---C---C---Me} \\ \quad \\ \text{OR} \quad \text{X} \end{array}$	CBrF ₃	193	41.0	37.2	-19.2	6
		Me	193	37.2	34.3	-16.7	6
		Et	193	41.8	35.6	-32.6	6
		Et	193	37.2	36.0	-7.1	6



Me ₃ C-CMe(OMe) ₂	CH ₂ CHCl	193	32.6	33.5	4.2	6
Me ₃ C-CMe ₂ (OMe)	CH ₂ CHCl	173	38.9			6
Me ₃ C-C(CD ₃) ₂ OH	CH ₂ CHCl	169	35.1			7
Me ₃ C-C(CD ₃)(C ₂ D ₅)OH	CH ₂ CHCl	163	37.2			7
Me ₃ C-C(CD ₃)(CH ₂ Ph)OH	CH ₂ CHCl	161	37.2			7
Me ₃ C-C(OMe ₃)(CD ₃)OH	CH ₂ CHCl	178	40.2			7
	Me ₂ O/DMF	178	39.7			7
	CH ₂ CHCl/					
	CD ₃ OD	183	40.6			7



CFCI ₃ /CS ₂	169	35.3	27.4	-46.9		8
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CFCI ₃ /CS ₂	156	31.3	28.1	-19.3		8
CFCI ₃ /CS ₂	220	47.3	42.5	-21.8		8



CBrF ₃	139	26.8	25.9	-4		9
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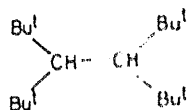
a. ΔG° and ΔH° are in kJ mol^{-1} ; ΔS° in $\text{J mol}^{-1} \text{K}^{-1}$.

b. T = coalescence temperature.

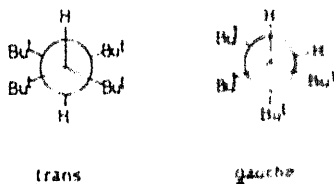
c. HCB = hexachlorobutadiene.

References: 1. Lunazzi *et al* (1977a); 2. Brownstein *et al* (1977); 3. Anderson and Pearson (1975); 4. Anderson *et al* (1976); 5. Anderson *et al* (1978); 6. Wang and Bushweller (1977); 7. Bushweller *et al* (1974b); 8. Dempster *et al* (1974); 9. Bushweller *et al* (1979).

When the methyl groups of the above compounds are replaced by even bulkier *tert*-butyl groups, *viz* in *sym*-tetra-*tert*-butylethane **2**,

**2**

the central C-C bond rotation becomes so hindered that effectively no internal rotation occurs below the temperature of its chemical decomposition (Brownstein *et al* 1966). It was also found that unlike other similar examples such as 2,3-dimethylbutane, compound **2** was found to take the *gauche* rather than the *trans* conformation

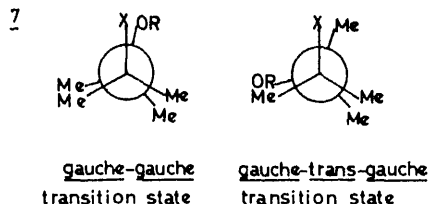


at room temperature. Because of the excessive strain between geminal *tert*-butyl groups as is suggested, the tetrahedral geometry of the tertiary carbons is distorted so that geminal alkyl groups are separated further. Such a distortion will destabilize the *trans* conformation while stabilizing the *gauche*, which is actually found to be favoured.

A large barrier to rotation was actually observed in another crowded compound 2,2,4,4,5,5,7,7-octamethyloctane **3** (see table 1), where a *trans* conformation is found to be more stable than a *gauche* by 0.18 kJ mol⁻¹ at 214 K, with a barrier to the central C-C bond rotation of 57.5 kJ mol⁻¹ (Anderson and Pearson 1975). In this case, however, the two *tert*-butyl groups are not close enough to each other for a direct steric hindrance to be effective in increasing the barrier. It is suggested that in an eclipsed transition state, the three substituents at either end of the ethane bond are compressed together due to steric and electrostatic repulsions between the eclipsing groups, producing enhanced interactions and thus resulting in the higher barrier to rotation.

It is not always clear whether a given interaction is steric or electrostatic in origin. If groups are separated by less than the sum of their van der Waals' radii, there is, by definition, some steric repulsion (Anderson *et al* 1976). The contribution of electrostatic attractive or repulsive forces to rotational barriers is subtle and has not been clearly defined (Sternhell 1975), though such interactions have been shown to be responsible for determining the conformational preference in polyhalogenoethanes (Anderson *et al* 1976). Examples of electrostatic repulsion in addition to van der Waals' interactions contributing to the rotational barriers were demonstrated by Wang and Bushweller (1977) in tetramethylethane, hexamethylethane, and octamethylethane.

for the *gauche* to *gauche* process as zero (figure 2). That is, the exchange process takes the *gauche-trans-gauche* route where the eclipsings between bonds of similar polarity are minimized.



In addition to the interaction between vicinal (1, 2) groups, 1,3-interactions have been shown to play an important role in determining relative conformational stabilities in substituted propanes. Dempster *et al* (1974) determined the activation parameters for internal rotation in three chloro-propanes at low temperatures. The results are included in table 1. The observed barriers to rotation are very similar to those of corresponding chloroethanes. Since eclipsed 1,3-groups are spatially much closer to

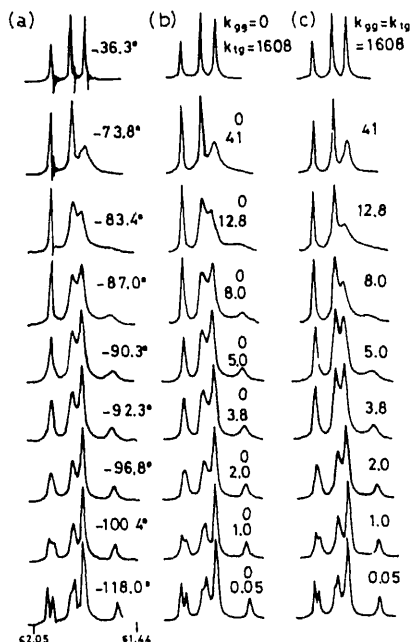
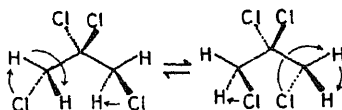


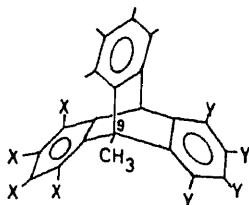
Figure 2. Experimental and theoretical ^1H DNMR spectra of 2-bromo-3-acetoxy-2,3-dimethylbutane (7, X = Br, R = COMe; 5% v/v in CH_2CHCl). (a) Experimental spectra (60 MHz) observed at various temperatures. (b) Theoretical ^1H DNMR spectra calculated as a function of the rate of *trans/gauche* equilibration assuming no *gauche* to *gauche* conversion. (c) Theoretical ^1H DNMR spectra calculated using equal rate constants for the *trans* to *gauche* and *gauche* to *gauche* processes. Reprinted with permission from Wang and Bushweller (1977). Copyright (1977) American Chemical Society.

each other than the eclipsed vicinal groups, the observed barriers may be interpreted in the sense that the reorientation of the terminal groups takes place in a cooperative fashion so as to avoid parallel 1,3-chlorine-chlorine interactions, as illustrated for 1,2,2,3-tetrachloropropane **10** below. A conformational analysis of some chloro-

**10**

loropropanes by Abraham and Loftus (1976) also suggests that, although 1,3-interactions are important, they are not the only decisive factor in conformational stabilities and that a *gauche* interaction between vicinal groups is similarly important (Bushweller *et al* 1979).

3.1b. *Other C(sp³)-C(sp³) rotations:* An unusually high barrier to methyl group rotation was found in substituted triptycenes **13**, where the 9-methyl group is surrounded by substituents at *peri* position, which are attached to a rigid tribenzenoid

**13**

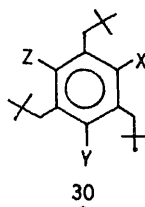
framework. Without any *peri* substituents, 9-methyl-triptycene (**13** with $X = Y = H$) has such a high molecular symmetry that the DNMR technique cannot be applied. The barrier E_a to methyl rotation in this molecule has been determined from the temperature dependence of the solid-state ¹H spin-lattice relaxation measurement to be 21.6 kJ mol⁻¹; as compared with theoretically calculated barriers of 16.3 kJ mol⁻¹ (MM1) and 20.1 kJ mol⁻¹ (CNDO/2) (Imashiro *et al* 1979). The large increase in the barrier to methyl rotation on substitution at *peri* positions, as shown in table 2, is, therefore, likely due to steric interactions.

However, the barriers do not show a straight correlation with the van der Waals' radii of the *peri* substituents, where the size of methyl group (2.0 Å) is supposed to be similar to that of bromine (1.95 Å). The observed barriers to rotation of the 9-methyl group in **13** and **14**, as well as the 9-isopropyl group in **15** and **16** (table 2) indicate that the effectiveness of substituents at *peri* positions for raising the barrier ($\Delta G^\ddagger$) decreases in the order Br > Cl > OCH₃ > CH₃, though the difference in solvents has to be taken

methyl group has been the subject of active discussions: a cogwheel-type rotation or gear effect between the methyl peri-substituent and the rotating 9-methyl or -isopropyl group has been proposed and disputed as the possible explanation (Hawkins *et al* 1971; Nakamura *et al* 1974a; Imashiro *et al* 1982). Other barriers measured in related systems are included in table 2.

Apart from the few exceptional cases as above, barriers to rotation about average $C(sp^3)-C(sp^3)$ single bonds are usually too small for the application of DNMR, which is generally limited to processes where $\Delta G^\ddagger$ is in excess of 20 kJ mol^{-1} . The barriers to methyl group rotation, for example, are less than 20 kJ mol^{-1} in most cases. Information on such fast molecular processes is contained in spin-lattice relaxation data. As mentioned in the preceding section, the practical use of T_1 data in the study of internal rotations is restricted by the difficulty in separating the observed T_1 into contributions from specific motions of molecules. Examples of measurements of barriers to methyl group rotation by a variable temperature T_1 method are included in table 2.

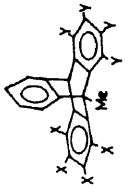
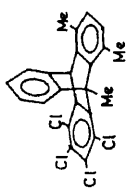
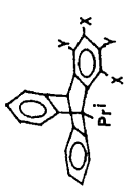
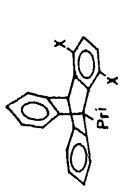
3.1c. *Aromatic and allylic hydrocarbons (sp^2-sp^3 and sp^2-sp^2):* Steric hindrance is the main factor in determining the barrier to internal rotation of the neopentyl groups around $C(sp^2)-C(sp^3)$ bonds in a very crowded aromatic system, 2,4,6-substituted 1,3,5-trineopentylbenzenes **30**. Carter *et al* (1975a) performed a complete bandshape



analysis of the methylene proton spectra of tribromotrimeopentylbenzene (**30** with $X = Y = Z = \text{Br}$) using an '8-sites program', by means of which all of the four conformations A, B, C and D have been taken into account (figure 3). The free energy of activation observed in chloroform- d solution was $\Delta G^\ddagger_{298\text{K}} = 71.1 \text{ kJ mol}^{-1}$ for $D \rightarrow A, B$ or C conversion, and 66.9 kJ mol^{-1} for the A, B , or $C \rightarrow D$ conversion. Values of activation parameters obtained for other derivatives of neopentyl-benzenes by this Swedish group of workers are summarized in table 3, which also includes data for several other systems found to demonstrate hindered internal rotation about aryl-alkyl and aryl-aryl carbon-carbon single bonds. Examples are 9-arylfluorenes **31–33**, polyarylbenzenes **34–36**, arylimines **37**, and arylcyclohexanones **38**.

Although these molecules present interesting and sometimes quite complex stereoisomerism, few data are available from measurements in different solvents or studies showing intermolecular interactions. Evidence of some solvent-solute interaction was indicated, however, in 2,4-dibromo-1,3,5-trineopentyl-6-nitrobenzene (**30**; $X = Y = \text{Br}$, $Z = \text{NO}_2$), in which the rotamer population ratio $D/A, C$ (see figure 3) was determined in various solvents, and found to increase from 0.44 in CHCl_2F to 1.12 in $\text{C}_6\text{H}_5\text{F}$. That is, the ground state energy of the archiral rotamers (D or B) seems to be preferentially stabilized in aromatic solvents. It is suggested that in rotamer D one side of the aromatic ring plane is essentially free from steric hindrance

Table 2. Barriers to internal rotation about the C(sp³)-C(sp³) bond in various compounds^a.

No.	Compound	Substituents	Solvent ^b	Rot. obsvd.	T (K)	$\Delta G_f^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
13.		$\begin{matrix} X & Y \\ H & H \\ Cl & H \\ Br & H \\ Cl & Cl \\ Cl & Br \end{matrix}$	$\begin{matrix} \text{Solid} \\ CCl_3/CS_2 \\ CCl_3/CS_2 \\ CCl_3/CS_2 \\ CCl_3/CS_2 \end{matrix}$	$\begin{matrix} C_9\text{-Me} \\ C_9\text{-Me} \\ C_9\text{-Me} \\ C_9\text{-Me} \\ C_9\text{-Me} \end{matrix}$	298 298 298 298 298	$\begin{matrix} 43.1 \\ 42.7 \\ 44.4 \\ 47.7 \end{matrix}$	$\begin{matrix} 21.6 (E_a) \\ 36.0 \\ 40.2 \\ 56.5 \\ 51.9 \end{matrix}$	$\begin{matrix} -24.7 \\ -8.8 \\ 41.0 \\ 14.2 \end{matrix}$	$\begin{matrix} 1 \\ 2 \\ 2 \\ 2 \\ 2 \end{matrix}$
14.			$\begin{matrix} CCl_3/CS_2 \end{matrix}$	$\begin{matrix} C_9\text{-Me} \end{matrix}$	298	46.9	50.6	12.6	2
15.		$\begin{matrix} H & Me \\ Cl & Cl \\ Br & Br \end{matrix}$	$\begin{matrix} TCE \\ HCB \\ HCB \end{matrix}$	$\begin{matrix} C_9\text{-Pr}^i \\ C_9\text{-Pr}^i \\ C_9\text{-Pr}^i \end{matrix}$	298 298 298	$\begin{matrix} 83.3 \\ 106.7 \\ 109 \end{matrix}$	$\begin{matrix} 72.0 \\ 125.9 \end{matrix}$	$\begin{matrix} 38.1 \\ 64.9 \end{matrix}$	$\begin{matrix} 3 \\ 3 \\ 3 \end{matrix}$
16.		$\begin{matrix} Me & OMe \\ Et & OMe \end{matrix}$	$\begin{matrix} CCl_3/CS_2/ \\ (CD_3)_2CO \\ HCB \\ HCB \end{matrix}$	$\begin{matrix} C_9\text{-Me} \\ C_9\text{-Et} \\ C_9\text{-Pr}^i \\ C_9\text{-Pr}^i \end{matrix}$	298 298 298 298	$\begin{matrix} 36.8 \\ 57.7 \\ 98.7 \\ 91.2 \end{matrix}$	$\begin{matrix} 30.1 \\ 59.8 \\ 103.8 \\ 89.5 \end{matrix}$	$\begin{matrix} -22.6 \\ 7.1 \\ 16.3 \\ 6.3 \end{matrix}$	$\begin{matrix} 2 \\ 4 \\ 3 \\ 3 \end{matrix}$
17.		$\begin{matrix} H & H \\ H & OMe \\ F & F \\ Cl & Cl \\ Br & Br \end{matrix}$	$\begin{matrix} CS_2/CH_2Cl_2 \\ CS_2 \\ CS_2/CH_2Cl_2 \\ CS_2/CH_2Cl_2 \\ CS_2/CH_2Cl_2 \end{matrix}$	$\begin{matrix} C_9\text{-Bu}^t \\ C_9\text{-Bu}^t \\ C_9\text{-Bu}^t \\ C_9\text{-Bu}^t \\ C_9\text{-Bu}^t \end{matrix}$	298 298 298 298 298	$\begin{matrix} 41.4 \\ 47.7 \\ 46.4 \\ 50.2 \\ 46.4 \end{matrix}$	$\begin{matrix} 29.7 \\ 42.7 \\ 31.8 \\ 42.3 \\ 51.9 \end{matrix}$	$\begin{matrix} -39.3 \\ -17.2 \\ -49.4 \\ -27.2 \\ 18.8 \end{matrix}$	$\begin{matrix} 5 \\ 5 \\ 5 \\ 5 \\ 5 \end{matrix}$

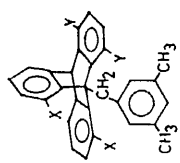
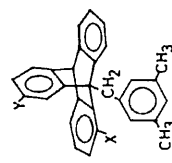
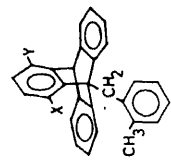
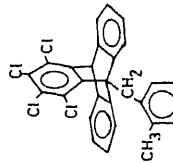
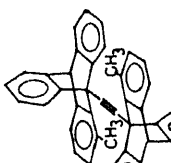
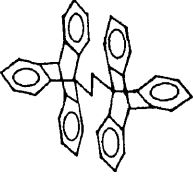
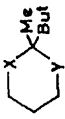
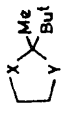
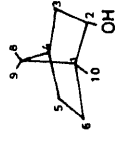
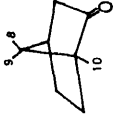
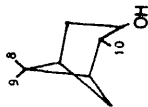
18.		Cl	Me	CDCl ₃	Ar-CH ₂	331	69.5	6
					C ₉ -CH ₂	334	103.8	6
					Ar-CH ₂	311	65.3	6
					C ₉ -CH ₂	440	92.5	6
					Ar-CH ₂	303	63.6	6
19.		Cl	H	CDCl ₃	C ₉ -CH ₂	324	65.7	6
					Ar-CH ₂	253	52.7	6
					C ₉ -CH ₂	245	51.9	6
					Ar-CH ₂	206	42.7	6
					Ar-CH ₂	202	41.8	6
20.		Cl	OMe	CS ₂	C ₉ -CH ₂	209	46.0	6
					Ar-CH ₂	276	56.5	7
					C ₉ -CH ₂	338	74.1	7
					Ar-CH ₂	287	59.0	7
					C ₉ -CH ₂	371	83.3	7
21.		Cl	H	C ₆ D ₅ Cl	Ar-CH ₂	282	57.3	7
					C ₉ -CH ₂	371	83.3	7
					Ar-CH ₂	286	58.2	7
					C ₉ -CH ₂	385	86.6	7
					Ar-CH ₂	283	63.1	8
22.					sc → ap			8
					ap → sc			8

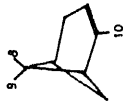
Table 2. (Continued)

No.	Compound	Substituents	Solvent ^b	Rot. obsvd.	T (K)	$\Delta G_f^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
23.					243	58.5			8
24.		O O O S	CH ₂ CHCl CH ₂ CHCl	C-Bu ^t C-Bu ^t	163.4 189.7	36.4 40.2	37.2 41.4	5.9 5.9	9 9
25.		O O S S O S	CH ₂ CHCl CH ₂ CHCl CBrF ₃ CH ₂ CHCl CBrF ₃	C-Bu ^t C-Bu ^t C-Bu ^t C-Bu ^t C-Bu ^t	148.5 203.0 140.0 172.0 133.6	31.4 44.4 31.4 41.0 29.3	31.4 46.4 31.4 45.2 28.9	0 10.5 0 23.0 -4.0	9 9 9 9 9
26.			CDCl ₃	8-Me 9-Me 10-Me	302 302 302	(V ₃) 12.5 10.5 16.3	8.9 8.2 7.2	-3 -3 -7	10 10 10
27.			CDCl ₃	8-Me 9-Me 10-Me	302 302 302	10.5 9.2 11.3	6.8 6.5 5.7	-9 -9 -12	10 10 10

28.

CDCl₃8-Me
9-Me
10-Me302
302
30210.0
9.6
15.95.3
6.7
8.3-13
-9
-1010
10
10

29.

CDCl₃8-Me
9-Me
10-Me302
302
30210.0
14.6
9.63.4
8.4
8.1-18
-6
-1010
10
10a. $\Delta G^\ddagger$ and $\Delta H^\ddagger$ are in kJ mol^{-1} ; $\Delta S^\ddagger$ in $\text{J mol}^{-1} \text{K}^{-1}$.

b. TCE = tetrachloroethane; HCB = hexachlorobutadiene.

References: 1. Imashiro *et al* (1979); 2. Nakamura *et al* (1974a); 3. Suzuki *et al* (1974); 4. Nakanishi and Yamamoto (1978); 5. Nakamura *et al* (1974b); 6. Yamamoto and Ōki (1979a); 7. Yamamoto and Ōki (1979b); 8. Mew and Vögtle (1979); 9. Stevenson *et al* (1974); 10. Ericsson *et al* (1980).

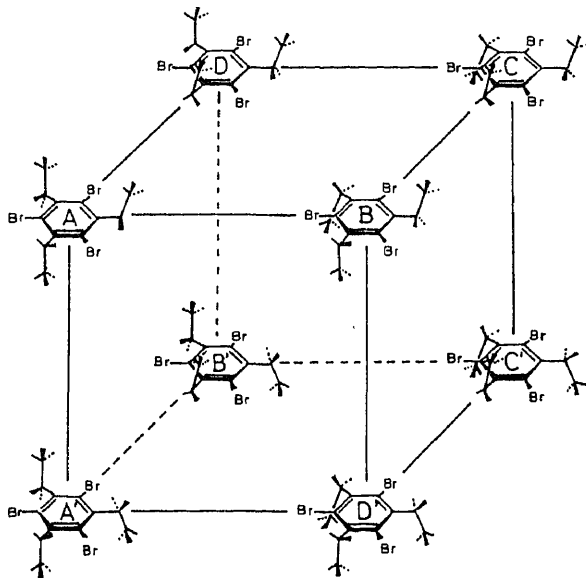
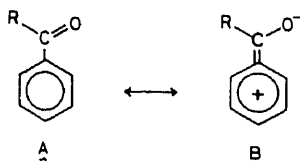


Figure. 3 The four rotamers and their interconversion scheme for 2,4,6-tribromo-1,3,5-trineopentylbenzene. Interconversions are assumed to occur *via* rotation of only one neopentyl group at a time. Reprinted with permission from Carter *et al* (1975). Copyright (1975) American Chemical Society.

allowing solvent molecules to approach for stronger interaction (Carter *et al* 1975a). Such stabilization of the ground state should, in effect, increase the barrier to interconversion of the rotamers, $D \rightarrow A, B, C$, in aromatic solvents relative to that in aliphatic solvents, though no experimental measurements of the barriers were given.

3.1d. Aromatic aldehydes and ketones (sp^2-sp^2): The internal rotation about the $\text{Ph}-\text{CO}$ bond of aromatic carbonyl compounds has received considerable attention because of the interest in the π -electron interaction between the aromatic system and the acyl group. The relatively high activation energy for internal rotation around this formally single carbon-carbon bond is due to its partial double bond character produced by delocalization of π -electrons and may be represented as the contribution from the resonance form **B**. Thus in the ground state, the carbonyl group is coplanar



with the ring system. Considering resonance form **B**, it is not surprising to find that the barrier height is readily modified by the presence of a substituent on the aromatic ring, especially in the *para*-position.

Proton NMR as well as IR and microwave measurements have mainly been used to

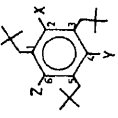
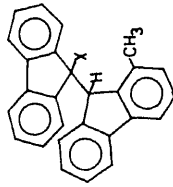
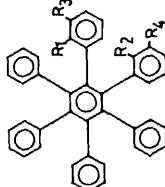
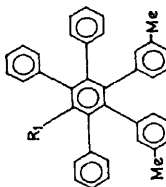
no.	Compound	X	Y	Z	Solvent	T(K)	$\Delta G_T^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
30.		Br	Br	Br	CDCl ₃	298	71.1	(D → A, B, C) (A, B, C → D)		1
		H	H	H	CDCl ₃	300	66.9			1
		H	H	Br	CF ₂ Cl ₂	118	19-22			2
		F	Cl	H	CF ₂ Cl ₂		22.6			3
		Cl	Cl	H			37.7			3
		Br	Br	H			59.8	60.7	2.5	4
		Me	Br	H	CDCl ₃		67.8	67.8	-0.4	4
		Me	Br	H	CDCl ₃		64.9	66.9	6.7	3
		I	Me	H	CDCl ₃		62.8	64.0	4.6	3
		NO ₂	I	H	CDBr ₃		77.0	73.2	-13.0	3
		Br	NO ₂	H	CDCl ₃	298	54.0	53.1	-3.3	3
		Br	NO ₂	H	CDCl ₃	298	60.2 (1)	55.6	-15.5	3
		Br			CDCl ₃		60.2 (3)	57.7	-8.4	3
		Br			CDCl ₃		60.2 (5)	57.3	-9.6	3
		H	Cl	NO ₂	CDCl ₃		61.1 (1)	63.6	8.8	3
		H	Cl		CDCl ₃		59.8 (5)	60.2	9.6	3
		H	Cl		CS ₂ -acetone -d ₆ (5:1)	187	35.5 (mp) ^c			11
		H	Br		CHCl ₂ F	174	31.8 (bu) ^c			11
		H	Br		CS ₂ -acetone -d ₆ (5:1)	219	41.7 (np)			11
		H	I		"	179	35.2 (bu)			11
		H	OCH ₃		"	249	47.8 (np)			11
		H	OCH ₃		"	182	35.3 (bu)			11
		H	OCOCH ₃		"	232	41.1 (np)			11
		H	OCOCH ₃		CHCl ₂ F	165	27.5 (bu)			11
		H	OCOCH ₃		CS ₂ -acetone -d ₆ (5:1)	200	36.8 (np)			11
		H	OSi(CH ₃) ₃		CHCl ₂ F	164	28.4 (bu)			11
		H	OSi(CH ₃) ₃		CS ₂ -acetone -d ₆ (5:1)	210	36.3 (np)			11
		H	OSi(CH ₃) ₃		CHCl ₂ F	171	34.3 (bu)			11

Table 3. (Continued)

No.	Compound	X	Y	Z	Solvent	T (K)	$\Delta G_f^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
		H	CH ₃		CS ₂ -acetone -d ₆ (5:1)	209	39.3 (np)			11
		F	F		CHCl ₂ F	158	27.9 (bu)			11
					"	132	25.8 (np)			11
		Cl	Cl		CDCl ₃	141	28.2 (bu)			11
		Cl	CH ₃		CS ₂ -acetone -d ₆ (5:1)	217	44.9 (bu)			11
					"	182	33.4 (np)			11
		Br	Br		CDCl ₃	231	49.7 (bu)			11
		Br	CH ₃		CS ₂ -acetone -d ₆ (5:1)	191	37.5 (np)			11
					"	211	43.3 (bu)			11
31.		H	H		C ₄ Cl ₆	476	> 109			5
		OH	H		C ₄ Cl ₆	406	87.0			6
		OH	Pr ⁱ		Dioxane	404	87.4			6
		Cl	Pr ⁱ		CCl ₄		63-71			6
32.		H	H	H	C ₄ Cl ₆	433	89.5			7
					C ₂ Cl ₄	389	78.2			5
					DMSO	333	74.5			8
			H	Me	C ₄ Cl ₆	439	139.3			6
					C ₄ Cl ₆ /TsOH	445	141.4			6
			OH	Me	C ₄ Cl ₆	443	> 108.8			6
			H	Me	C ₄ Cl ₆	388	82.0			9
33.		Ph			CDCl ₃	233	48.5			10
		4-MePh			CDCl ₃	233	48.5			10
		3-MePh			CDCl ₃	233	49.0			10
					CDCl ₃	233	50.4			10

	CDCl ₃	233	48.5	10
	CDCl ₃	233	48.5	10
	CDCl ₃	233	49.0	10
	CDCl ₃	286	59.4	10
	CDCl ₃	280	60.2	10



34.		$\begin{matrix} R_1 & R_2 & R_3 & R_4 \\ OMe & Me & H & H \\ Me & Me & H & H \\ H & H & Me & Me \end{matrix}$	419	136.8 (A $\rightarrow$ B) ^b 137.2 (B $\rightarrow$ A) 157.3 (A $\rightarrow$ B) 159.4 (B $\rightarrow$ A) 68.6	12 12 12 12 12
35.		$\begin{matrix} H \\ Ph \\ Pr^i \\ Me \\ Et \\ CH(OH)CH_3 \\ Bu^t \end{matrix}$	288 293 293 293 293 293 293	64.9 72.4 70.3 67.8 67.4 68.6 78.2	13 13 14 14 14 14 14

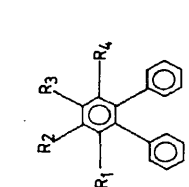
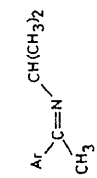
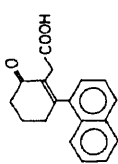
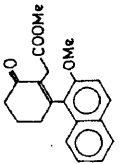
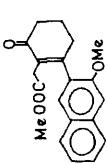
36.		$\begin{matrix} R_1 & R_2 & R_3 & R_4 \\ OMe & Me & H & H \\ Me & Me & H & H \\ H & H & Me & Me \end{matrix}$	294 294 419	71.1 71.5 136.4 (A $\rightarrow$ B) ^b 136.8 (B $\rightarrow$ A)	13 13 13 13
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Table 3. (Continued)

No.	Compound	X	Y	Z	Solvent	T (K)	$\Delta G_T^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
37.		Ar	2-CH ₃ C ₆ H ₄ 2-C ₆ H ₅ C ₆ H ₄ 2-NO ₂ C ₆ H ₄ 2-CH ₃ OC ₆ H ₄ 1-naphthyl		toluene-d ₈ " " " "	347 336 329 267 355	76.6 74.1 74.1 60.2 85.4			15 15 15 15 15
38.					PhNO ₂ Ph ₂ O CDCl ₃ C ₂ HCl ₅ CHBr ₃ CDCl ₃	438	91.6			16 16 16 16 16
38.					CDCl ₃	318	66.1			16
					CHCl ₂ CCl ₃	323	66.5			16

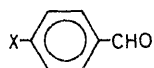
a. $\Delta G^\ddagger$ and $\Delta H^\ddagger$ are in kJ mol⁻¹; $\Delta S^\ddagger$ in J mol⁻¹ K⁻¹.

b. A and B are two rotational isomers.

c. np: neopentyl rotation; bu: *tert*-butyl rotation.References: 1. Carter *et al* (1975a); 2. Andersson *et al* (1980); 3. Nilsson *et al* (1974); 4. Carter *et al* (1970); 5. Siddall and Stewart (1969); 6. Ford *et al* (1975); 7. Kajigaeshi *et al* (1979); 8. Bartle *et al* (1970); 9. Kajigaeshi *et al* (1979); 10. Fujisaki *et al* (1976); 11. Andersson

CNMR, particularly because of the simplicity of the spectra. Drakenberg and workers have made extensive studies on the barriers to internal rotation in aromatic aldehydes and ketones and have recently summarized the available data (Drakenberg *et al.* 1980). The rotational barriers in *para*-substituted benzaldehydes **39** and acetophenones **40** are listed in tables 4 and 5, respectively.

Table 4. Barriers to internal rotation in *para*-substituted benzaldehydes **39**^a.



Substituent (X)	Method	Solvent	$\Delta G^\ddagger$ ^b	$\Delta H^\ddagger$ ^b	$\Delta S^\ddagger$ ^c	$V_2^\ddagger$	Reference
Me	¹ H NMR	CH ₂ Cl ₂	45.2				1
	¹ H NMR	CH ₂ Cl ₂	44.8	46.5			2
	¹ H NMR	PhCD ₃	43.9				3
	¹ H NMR	CH ₂ CHCl	42.7				3
	¹³ C NMR	CD ₂ Cl ₂	43.9	41.9	-10		4
	¹³ C NMR	C ₆ D ₅ CD ₃	41.4	25.1	-80		4
	¹³ C NMR	CHCl ₂ CCl ₂ F	44.9	46.6	7		5
	IR					55.7	6
Me	¹ H NMR	CH ₂ Cl ₂ /C ₂ F ₄ Br ₂	38.9				2
	¹ H NMR	PhCD ₃	39.3				3
	¹ H NMR	CH ₂ CHCl	38.5				1
	¹³ C NMR	CD ₂ Cl ₂	37.5				4
	¹³ C NMR	C ₆ D ₅ CD ₃	34.3	27.2	-30		4
	¹³ C NMR	CHCl ₂ F/CCl ₂ F ₂	37.7	38.7	6		5
	T ₁			36.25			7
	IR					37.8	6
	¹ H NMR	CH ₂ ClCH ₂ CHCl	35.0				2
	¹³ C NMR	CHCl ₂ F/CCl ₂ F ₂	34.1	35.2	5		5
	IR					26.7	8
	¹³ C NMR	CHCl ₂ F/CCl ₂ F ₂	34.0	32.5			5
	¹³ C NMR	CH ₃ ClCH ₂ CHCl	35.2				2
	¹³ C NMR	CHCl ₂ F/CHClF ₂	33.6				5
	IR					21.9	9
	¹³ C NMR	CHCl ₂ F/CCH ₂ F ₂	32.3				10
	IR					19.2	8
	IR					20.4	6
	IR					15.6	6
	¹ H NMR	CH ₂ Cl ₂	33.0				1
	¹³ C NMR	(CH ₃) ₂ O	32.2	34.7	15		11
	¹³ C NMR	CHCl ₂ F/CHClF ₂	31.7				10
	¹³ CT ₁			30.5			7
		Microwave gas phase				20.5	12
	IR					28.4	6
	IR	Gas phase				20	8
	IR					28.0	8

Table 4. (Continued)

Substituent (X)	Method	Solvent	$\Delta G^{\neq b}$	$\Delta H^{\neq b}$	$\Delta S^{\neq c}$	ν_2^b	Reference
CF ₃	¹³ C NMR	CHCl ₂ F/CHClF ₂	28.0				10
CHO	¹³ C NMR	CHCl ₂ F/CHClF ₂	28.8				5
CN	¹³ C NMR	CHCl ₂ F/CHClF ₂	28.5				5
NO ₂	¹³ C NMR	CHCl ₂ F/CHClF ₂	27.7				5
	IR					18.1	6
OCF ₃	¹³ C NMR	CHCl ₂ F/CHClF ₂	32.0				5

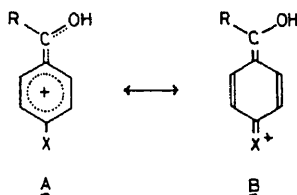
a. From Drakenberg *et al* (1980), reproduced by permission of Royal Society of Chemistry.

b. In kJ mol⁻¹.

c. In J mol⁻¹ K⁻¹.

References: 1. Anet and Ahmad (1964); 2. Grindley *et al* (1975); 3. Klinck *et al* (1967); 4. Klinck and Stothers (1976); 5. Drakenberg *et al* (1980); 6. Campagnaro and Wood (1970); 7. Doddrell *et al* (1979); 8. Miller *et al* (1967); 9. Silver and Wood (1964); 10. Drakenberg *et al* (1974a); 11. Lunazzi *et al* (1975); 12. Kakar *et al* (1970); 13. Hehre *et al* (1972); 14. Liljefors and Allinger (1976).

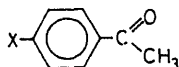
They have shown that the energy of the rotational barrier correlates well with the Hammett constant of the *para*-substituents (Drakenberg *et al* 1980). Among various parameters attempted, a set of dual parameters σ_I and σ_R^+ gave the best correlations, indicating contributions from both inductive and resonance effects. It was also noted that the protonation increased the sensitivity to the *para*-substituent effect. Proton NMR spectra of protonated benzaldehydes and ketones **41** (R = H, CH₃ or



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C₂H₅) were observed with the compounds dissolved in so-called Magic Acid (FSO₃H–SbF₅–SO₂ClF) at –40°C (Sommer *et al* 1976a, b), and the free energy of activation to internal rotation about the Ph–CRO bond became almost twice as high as that of the corresponding free aldehydes (table 6), indicating an increased contribution from the structure **B** of **41**.

Some of the rotational barriers shown in table 4 and 5 have been estimated for the case of the gas phase by IR or microwave techniques. The gas-phase barriers of benzaldehyde and acetophenone, for example, are all found to be lower than those obtained in the liquid phase and are also in good agreement with the results of force field calculations. Although most studies on substituted aromatic carbonyl compounds have been conducted in relatively 'inert' solvents as may be seen in these tables, the difference between the gas-phase and the liquid phase values may be explained as the

Table 5. Barriers to internal rotation in *para*-substituted acetophenones **40**^a.

Substituent (X)	Method	Solvent	$\Delta G^\ddagger$ ^b	ν_2^b	Reference
NMe ₂	¹ H NMR	CH ₂ Cl ₂ /CH ₂ CHCl	34.7		1
	¹ H NMR	PhCD ₃	35.6		2
OMe	¹ H NMR	CH ₂ Cl ₂ /CH ₂ CHCl	27.6		1
	¹ H NMR	PhCD ₃	30.5		2
	¹ H NMR	CH ₂ CHCl	27.2		2
	¹³ C NMR	CHClF ₂ /CHCl ₂ F	28.6		3
Me	¹³ C NMR	CHClF ₂ /CHCl ₂ F	24.7		3
F	¹³ C NMR	CHClF ₂ /CHCl ₂ F	24.7		3
	IR	Gas phase		14.6	4
Cl	¹³ C NMR	CHClF ₂ /CHCl ₂ F	22.7		3
Br	¹³ C NMR	CHClF ₂ /CHCl ₂ F	22.6		3
H	¹³ C NMR	CHClF ₂ /CHCl ₂ F	22.4		3
	IR	Gas phase		13.0	4
	<i>Ab initio</i>			18.4	5
	Force field			13.1	6
CF ₃	¹³ C NMR	CHClF ₂ /CHCl ₂ F	19.7		3
NO ₂	¹³ C NMR	CHClF ₂ /CHCl ₂ F	18.4		3

a. From Drakenberg *et al* (1980), reproduced by permission of Royal Society of Chemistry.

b. In kJ mol⁻¹.

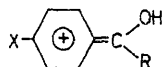
References: 1. Klinck and Stothers (1967); 2. Klinck *et al* (1967); 3. Drakenberg *et al* (1976); 4. Miller *et al* (1967); 5. Hehre *et al* (1972); 6. Liljefors and Allinger (1976).

solvent tends to stabilize the relatively polar ground state more than the transition state (Drakenberg *et al* 1980).

When the carbonyl group is bonded to a molecular residue lacking in symmetry about the bond, the ground state will consist of two different conformations, which often are frozen at low temperature, and the problem of conformational assignment arises. This is the case with *ortho*- and *meta*-substituted benzaldehydes and many heterocyclic aldehydes and ketones.

The relative ground state energies of the conformations and thus the preferred orientation of the carbonyl group with respect to the ring substituents seem to be determined by several factors including the dipole-dipole interaction between the carbonyl group and the ring substituents, steric repulsions, intramolecular hydrogen bonds and solvent effects.

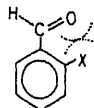
The steric effect is clearly observed in the study of Lunazzi *et al* (1976a) on a series of *ortho*-substituted benzaldehydes **42**, where X = H, Me, Et, Prⁱ and Bu^t (see table 7). The larger the substituent X, the smaller the population of the *O-cis* isomer. That is, the ground state of the *O-cis* isomer becomes destabilized as the size of the substituent X



Substituent (X)	$\Delta G^\ddagger$ in kJ mol ⁻¹		
	Benzaldehydes ^b (R = H)	Acetophenones ^c (R = Me)	Propiophenone ^d (R = Et)
OMe	78.0	61.4	.
Me	67.4	54.2	49.3
Et	66.3		47.7
Pr ⁱ	66.1		49.0
Bu ^t	65.7		49.8
F	64.7	50.9	48.1
Cl	60.8	49.1	43.9
Br	60.6	48.9	43.1
H	61.3	48.1	43.1
CF ₃	49.5	39.8	
NH ⁺ Me	45.2		
OH ⁺ Me	54.0	41.4	
CHOH ⁺	41.2		

a. From Drakenberg *et al* (1980), reproduced by permission of Royal Society of Chemistry.

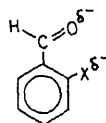
b. Sommer *et al* (1976a); c. Barthelemy *et al* (1978); d. Drakenberg *et al* (1980).



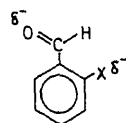
42

perpendicular transition states are unaffected. As a result, the conjugation between CHO and the benzene ring is reduced and thus the free energy of activation $\Delta G^\ddagger$ is decreased with the increase in the substituent size.

Dipole-dipole repulsions between bonds of similar polarity and attractions between those of opposite polarity may explain the observed population ratio of *ortho*- and *meta*-substituted benzaldehydes (table 7). No O-*cis* isomers were found in ¹³C NMR spectra of 2-fluoro- and 2-chloro-benzaldehydes **42** at any temperatures, and thus the



O-cis



O-trans

Table 7. Barriers to internal rotation in *ortho*- and *meta*-substituted aromatic aldehydes^a.

No.	Compound	X	O- <i>cis</i> / O- <i>trans</i>	Solvent	T (K)	$\Delta G^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
42.		H	50:50	CHF ₂ Cl		32.2			1
		Me	36:64	CHF ₂ Cl		28.6			1
		Et	25:75	CHF ₂ Cl		26.9			1
		Pr ⁱ	15:85	CHF ₂ Cl		24.7			1
		Bu ^t	0:100	CHF ₂ Cl		—			1
		Me	50:50	CF ₂ Cl ₂ /CHFCl ₂	123	27.0			2
43.		F	0:100	CF ₂ Cl ₂ /CHFCl ₂	123	—			2
		Cl	0:100	CF ₂ Cl ₂ /CHFCl ₂	123	—			2
		Me	55:45	CF ₂ Cl ₂ /CHFCl ₂	123	33.0			2
		F	64:36	CF ₂ Cl ₂ /CHFCl ₂	123	30.7			2
		Cl	65:35	CF ₂ Cl ₂ /CHFCl ₂	123	31.9			2
		Br	59:41	CF ₂ Cl ₂ /CHFCl ₂	123	33.0			2
44.		H	10:10:79 (<i>tc:ct:cc</i>)	(CD ₃) ₂ CO/Et ₂ O-d ₁₀	178	41.4	(<i>cc</i> → <i>tc</i> , <i>cc</i> → <i>ct</i>)		3
		EtO		(CD ₃) ₂ CO/Et ₂ O-d ₁₀	193	40.0	41.8	8.4	3
45.		H			215.6	41.8	37.4	-21	4
		OMe			207.5	40.2	41.8	8	4
		OEt			222.1	43.1	41.1	-9	4
		OPr			227.1	44.1	38.4	-25	4
46.		CN		CHFCl ₂ /CHF ₂ Cl	188	35.1			5
		F		CHFCl ₂ /CHF ₂ Cl	147	29.3			5
		Cl		CHFCl ₂ /CHF ₂ Cl	143	26.8			5
		Br		CHFCl ₂ /CHF ₂ Cl	138	25.5			5

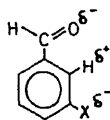
Table 7. (Continued)

No.	Compound	X	O-cis/ O-trans	Solvent	T (K)	$\Delta G^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
47.		4-CHO	1:1	CHCl ₃ /CF ₂ Cl ₂		24.7			6
				CHCl ₃ /CF ₂ Cl ₂		26.4			7
		3-CHO	1:4	CHCl ₃ /CF ₂ Cl ₂		30.1			6
			1:4	Me ₂ O		29.9			7
			27:73	CHF ₃ Cl		31.5			7
		2-CHO	1:16	CHCl ₃ /CF ₂ Cl ₂		31.4			6
			7:93	CHCl ₃ /CF ₂ Cl ₂		32.2			7

a. $\Delta G^\ddagger$ and $\Delta H^\ddagger$ are in kJ mol⁻¹; $\Delta S^\ddagger$ in J mol⁻¹ K⁻¹.

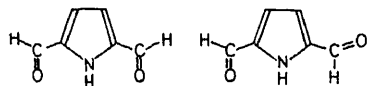
References: 1. Lunazzi *et al* (1976a); 2. Drakenberg *et al* (1975); 3. Farnier and Drakenberg (1975); 4. Hirota *et al* (1977); 5. Anet and Ghiaci (1979b); 6. Drakenberg (1976a); 7. Lunazzi *et al* (1976b).

substituted derivatives by the inductive effect of the substituent produces a more positive proton at the *ortho*-position resulting in the *O-cis* form being slightly more stable (Drakenberg *et al* 1975).



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A similar but more pronounced effect was observed in pyrroldialdehydes **44**, which exists as about 80 % *cis-cis* and 20 % *cis-trans* with no *trans-trans* being found (Farnier and Drakenberg 1975).

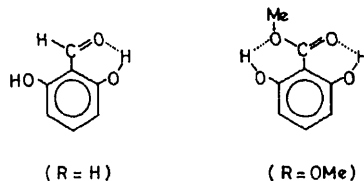


NO-*cis-cis* (cc)

NO-*cis-trans* (ct)

44

Hirota *et al* (1977) examined the effect of intramolecular hydrogen bonding on the barrier to rotation in 2,6-dihydroxybenzaldehyde and related benzoates, **45**. Larger rotational barriers were indeed found for these compounds as compared with the 2,6-unsubstituted derivative, indicating the stabilization of the planar ground state conformation by intramolecular hydrogen bonding.



(R = H)

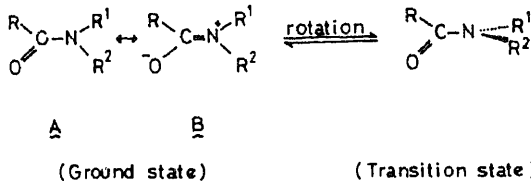
(R = OMe)

45

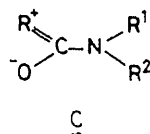
Barriers observed in other aromatic aldehydes are also included in table 7.

3.2 Carbon-nitrogen bonds

3.2a. Amides and thioamides: The origin of the rotational barrier around the C-N bond of amides is associated with its partial double bond character. It arises from resonance interaction between the lone pair of electrons on the nitrogen atom and the carbonyl π system. The energy barrier to rotation is, therefore, primarily determined by the π -bond order. It is readily conceivable then that the electronic effect of substituent R, as well as its conjugative ability, will greatly influence the value of the rotational barrier. When an electronegative substituent R effectively withdraws electron density from the carbonyl carbon, it enhances the delocalization of the nitrogen lone pair. As a result, the planar ground state is stabilized and the barrier to rotation is increased. Thus,



a trifluoromethyl group when it replaces methyl on the α -carbon of dimethylacetamide increases the free energy of activation from 72.8 to 75.5 kJ/mol (Table 8). On the other hand, an electron donor and a substituent that conjugate with the carbonyl group is effective in reducing the contribution of resonance form **B** and so lowers the rotational barrier. This latter situation is considered as an increased contribution from resonance structure **C**, in which



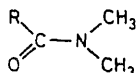
the electron system is confined to the $\text{O}=\text{C}-$ region of the molecule, decreasing the $\text{C}-\text{N}$ bond order. The electron-releasing and hyper-conjugative ability of alkyl substituents seems to work in this way as demonstrated by the decreasing $\Delta G^\ddagger$ values for rotation in the order $\text{R}=\text{H}, \text{CH}_3, \text{CH}(\text{CH}_3)_2$ and $\text{C}(\text{CH}_3)_3$ of N,N-dimethylamides (Table 8), although a steric effect may also play a large part in this case.

In general, a steric factor contributes by destabilizing the planar ground state. A bulky substituent at the carbonyl carbon or the nitrogen will decrease the barrier to rotation.

Substituent effects on the rotational transition state rather than on the ground state have been suggested as the interpretation of the observed trends in the barriers of N,N-dimethylamides **1**, such as decreasing order of barrier height $\text{R} = \text{F} > \text{Cl} > \text{Br}$. According to Bingham (1975), the larger effect due to lone pair-polar bond conjugation of Br compared to F stabilizes the transition state and thus lowers the barrier. However, as noted by Kornberg and Kost (1979), the three effects, that is, transition state hyper-conjugation, the steric ground state destabilization and the electronic effect, operate in the same direction and are not easily separable in the barriers in amides, and may each contribute to some extent to the observed results for a series of $\text{R} = \text{F}, \text{Cl},$ and Br .

The general tendencies of all these substituent effects have been extensively studied, especially for N,N-dimethylamides and are well summarized by Jackman (1979).

Wunderlich *et al* (1978) investigated a linear free energy relationship for the substituent effect in terms of steric inductive and resonance parameters. The parameters used for the steric effect were Charton's ν value, E_s values and van der Waals' radii calculated for a variety of different conformations of the substituents. For twenty-two α -substituted N,N-dimethylamides, including such substituents as halomethyl-, halophenyl-, methoxy- and cyano-groups, they obtained reasonable correlations by the regression equation ($r = 0.903$)

Table 8. Barriers to internal rotation in N,N-dimethyl substituted aliphatic amides^a.

No.	Substituent (R)	Solvent ^b (Conc.)	T _c (K)	E _a	ΔG ₂₉₈ [‡]	ΔH [‡]	ΔS [‡]	Reference
1.	H	Neat		89.1	87.4		-5.9	1
		Decalin		85.4	84.9		10	1
	D	Neat		90.4	88.7		-4.2	2
		Neat		101.7	91.2		26.4	15
	CH ₃	Neat		75.9	75.7		2.9	1
	CD ₃	CCl ₄		76.6	72.8		4.6	3
	C ₂ H ₅	Neat	326		72.0	66.9	-17	1
		CCl ₄ (10%)	325.4	70.7	72.0	68.2	-13	4
		Acetone (10%)	323		71.1	64.4	-22	1
	(CH ₃) ₂ CH	C ₆ H ₅ Cl (10%)	304.5	61.1	69.0	58.6	-33.5	4
	(CH ₃) ₃ C	C ₆ H ₅ CH ₃ (30%)	210.3	59.0	43.9	56.5	42	4
	CH ₂ =CH	Neat			67.4 ^c			5
	CH ₃ CH=CH	CDCl ₃ (0.5 M)	267		62.3	37.7	-84	6
	C ₆ H ₅ CH=CH	CDCl ₃ (0.5 M)	303.8		67.6	59.0	-28.5	7
		CDCl ₃ (0.25 M)	312		68.6	72.0	11.5	8
	HC≡C	TCE (0.5 M)	377		81.8 ^c			9
	CH ₃ C≡C	TCE (0.5 M)	377.1		80.8	76.1	-14.6	9
			380.4 ^d		82.0 ^d	82.8 ^d	2.5 ^d	9
	C ₆ H ₅ C≡C	TCE (0.5 M)	376.6		81.9	73.2	-23	9
	F	CCl ₄ (16.5 m%)	318	76.6	75.7	74.1	-6	10
	Cl	CCl ₄ (6%)		71.5	69.0	69.0	-2.5	11
		Neat		73.6	70.3	71.5	3	11
	Br	Neat		64.0	65.7	61.5	-14	11
	(CH ₃) ₂ ClC	C ₆ H ₅ Cl (30%)	264.4	58.2	56.9	55.6	-4	4
	(CH ₃)Cl ₂ C	C ₆ H ₅ Cl (30%)	302.5	69.0	64.4	66.5	8	4
	FCH ₂	C ₆ H ₅ Cl (30%)	317.5		71.1 ^c			4
	F ₂ CH	C ₆ H ₅ Cl (30%)	348.1		78.7 ^c			4
	F ₃ C	CCl ₄ (11 m%)		72.7	75.5	70.2	-17.8	12
		TCE			78.7			13
	ClCH ₂	C ₆ H ₅ Cl (10%)	293.5	66.9	68.6	64.4	-17	4
	Cl ₂ CH	C ₆ H ₅ Cl (30%)	319.9	79.9	73.6	77.4	13	4
	Cl ₃ C	C ₆ H ₅ Cl (10%)	285.3	64.0	62.3	61.5	2	
	BrCH ₂	C ₆ H ₅ Cl (30%)	292.2	72.4	66.1	69.9	13	4
	Br ₂ CH	C ₆ H ₅ Cl (30%)	317.5	68.6	72.4	66.5	-21	4
	Br ₃ C	Acetone (30%)	277.9	56.9	58.6	54.4	-13	4
2.	CH ₃ COCH ₂							
	DMAA (keto)	CCl ₄ (4m%)			72.8		15	14
	DMAA (enol)	CCl ₄ (4m%)			68.6		-6	14

a. ¹H DNMR results observed at 60 MHz unless noted otherwise. E_a, ΔG[‡] and ΔH[‡] are given in kJ mol⁻¹; ΔS[‡] in J mol⁻¹ K⁻¹.

b. TCE = tetrachloroethane (CHCl₂CHCl₂).

c. Obtained by approximate method at coalescence temperature.

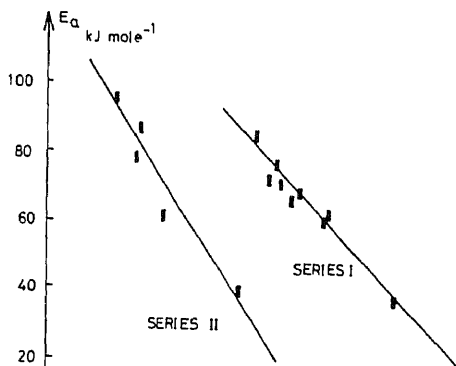
d. Result obtained at 100 MHz.

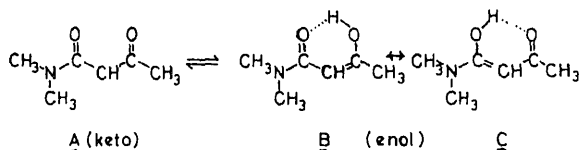
References: 1. Drakenberg *et al.* (1972); 2. Rao *et al.* (1977); 3. Neuman and Jonas (1974b); 4. Wunderlich *et al.*

where the terms represent the inductive (σ_I), steric (ν) and resonance (σ_{R-}) parameters, respectively. The size of the coefficients, a , b , and c , indicate the relative importance of those parameters. Thus, in the halogen series with F, Cl and Br as the α -substituents, the inductive effect is found as important as the steric effect, whereas the inclusion of the other substituents in the analysis leads to an increase in the relative importance of the steric and resonance factors. The correlation was obtained for the values of $\Delta G^\ddagger$ to within $\pm 3.3 \text{ kJ mol}^{-1}$ ($\pm 0.8 \text{ kcal mol}^{-1}$) of the corresponding experimental values.

The possibility of evaluating the rotational energy barrier to amide C-N bond rotation through the ^{15}N chemical shift has been examined by Martin *et al* (1977). It is reasonable to expect some correlation between the activation energy E_a and $\delta^{15}\text{N}$ since the ^{15}N chemical shift is known to be determined primarily by a paramagnetic term, which is strongly dependent on the amount of π bonding at the nitrogen atom, and the barrier for C-N rotation is also dependent on the amount of π bonding. Good correlations were obtained between $\delta^{15}\text{N}$ and E_a within homogeneous series of compounds, amides and thioamides; that is, different correlation lines were required for different classes of compounds, as indicated in figure 4.

Correlations between $\Delta G^\ddagger$ or E_a and the chemical shifts of ^{15}N and other nuclei, such as ^{14}N , ^{17}O and $^{13}\text{C=O}$, in amides were further investigated by Jones and Wilkins (1978) and by Su (1978). Linear relationships were observed among these chemical shifts when the carbonyl substituents were limited to closely related substituent groups. Su (1978) suggests that linear correlation between E_a for the C-N bond rotation and the chemical shifts of various nuclei of the amide exists only when the observed chemical shift is primarily determined by the amount of nitrogen lone pair delocalization and is not affected by the direct conjugation with substituent groups. In other words, the rotational barrier may be correlated linearly with $\delta^{15}\text{N}$, but not with $\delta^{13}\text{C=O}$, when carbonyl substituents are changed, whereas $\delta^{13}\text{C=O}$ and $\delta^{17}\text{O}$ may be related linearly, but $\delta^{15}\text{N}$ may not, when nitrogen substituent groups are changed. Because of these complications, and also because different correlation lines are required for different classes of compounds, it has been recommended that barriers be determined, whenever



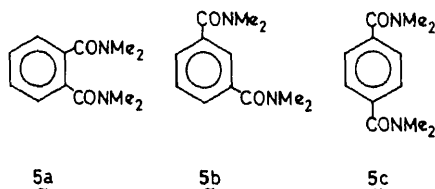


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the scale, that the temperature dependence on N-CH₃ signals of the keto and enol forms could be studied separately. Thus, in the enol form, the π electron conjugation is identically localized at the chelated enol ring, substantially reducing the C-N double bond character. The $\Delta G^\ddagger$ for the internal C(O)-N bond rotation of the enol form was 10 kJ mol⁻¹ smaller than that of the keto form. The results of the activation parameters are included in table 8.

A substituent at the *ortho* position of aromatic amides may produce a large effect on the amide C-N rotational barrier either sterically or through intramolecular hydrogen bonding. When the *ortho*-substituent is a halogen or a methyl, the barrier to rotation is generally increased (see table 9, compound 4). Fong *et al* (1978b) examined the substituent effect by a multi-substituent parameter method and revealed, as expected, that the increase is mainly due to a large steric effect, with resonance and inductive effects being less important.

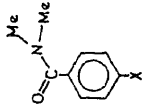
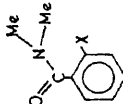
An interesting example of a large steric effect was given by Spassov *et al* (1974b) who reported the barriers to C-N bond rotation in three phthalic tetramethylamides **5**. Results of the activation parameters are listed in table 9. Upon comparison with the $\Delta G^\ddagger$ value of unsubstituted N,N-dimethylbenzamide, the values of *meta*- and *para*-substituted derivatives, **5b** and **5c**, agree very well, confirming that the kinetic process involved is that of the C-N bond rotation of the amide groups, rather than ring carbon-carbonyl carbon rotation. The increase in $\Delta G^\ddagger$ for the *ortho* compound **5a**, then, is entirely due to the steric hindrance created by the crowded substituents.

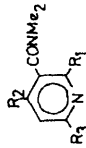
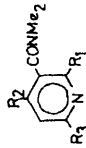


A similar increase in $\Delta G^\ddagger$ was observed in *ortho*-methyl substituted nicotinamides **6**, where a second *ortho*-methyl produced an increase more than twice that due to the first *ortho*-substitution (Sattler and Schunack 1975).

When an amino- or a hydroxy-group is introduced at the *ortho* position of aromatic amides, the amide rotational barrier is reduced dramatically (*cf.* table 9, Compound 7). This phenomenon is usually explained by the formation of intramolecular hydrogen

Table 9. Barriers to internal rotation in *N,N*-dimethyl aromatic amides^a.

No.	Compound	Substituent (X)	Solvent	<i>T</i> (K)	$\Delta G_T^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
3.		H	CDCl ₃	298	65.31			1
			CDCl ₃	298	66.5			2
		CMe ₃	CDCl ₃	298	61.97	86.2	84.3	1
		Me	CDCl ₃	298	62.09	82.5	68.0	1
		CH ₂ Br	CDCl ₃	298	64.39	82.5	60.6	1
		CHBr ₂	CDCl ₃	298	64.60	82.4	59.7	1
		CBr ₃	CDCl ₃	298	65.31	79.5	47.7	1
		F	CDCl ₃	298	63.76			
		Cl	CDCl ₃	298	65.44			
		Br	CDCl ₃	298	65.19			
4.		F	CDCl ₃	373	73.49	84.0	28.1	3
			CD ₃ CN	373	73.67	80.7	19.0	3
		Cl	CDCl ₃	373	79.72	88.2	22.7	3
			CD ₃ CN	373	80.01	81.2	3.2	3
		Br	CDCl ₃	373	80.58	78.1	-6.7	3
			CD ₃ CN	373	81.34	77.6	-10.0	3
		I	CDCl ₃	373	80.75	81.5	0.7	3
			CD ₃ CN	373	81.34	85.8	12.0	3
		Me	CDCl ₃	373	72.11	92.1	53.4	3
			CD ₃ CN	373	73.94	74.9	2.6	3
5.		H	CDCl ₃	373	64.41	71.2	18.3	3
			CD ₃ CN	373	63.47	70.3	18.4	3
			<i>T_c</i> (K)		$\Delta G_{T_{58}}^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	
		5a <i>o</i> -C ₆ H ₄ (CONMe ₂) ₂	CDCl ₃	319	71.17	72.4	3.8	4
		5b <i>m</i> -C ₆ H ₄ (CONMe ₂) ₂	CDCl ₃	295	65.52	59.4	-20.5	4
		5c <i>p</i> -C ₆ H ₄ (CONMe ₂) ₂	CDCl ₃	298	65.35	67.8	8.8	4

No.	Compound	Substituent			Solvent	Method	T_c (K)	$\Delta G^\ddagger$	Reference	
6.		$\underline{R_1}$	$\underline{R_2}$	$\underline{R_3}$						
		H	H	H	Water	^1H (TLS) ^b	344	76.9	5	
					CDCl ₃	^1H (Tc) ^c	301	65.9	6	
					C ₂ D ₂ Cl ₄	"	304	66.6	6	
		CH ₃	H	H	C ₂ D ₂ Cl ₄	"	345	73.1	6	
					DMSO	"	347	74.1	6	
		H	CH ₃	H	CDCl ₃	"	339	71.9	6	
		H	H	CH ₃	C ₂ D ₂ Cl ₄	"	298	65.7	6	
		CH ₃	CH ₃	H	DMSO	"	434	92.7	6	
		CH ₃	H	CH ₃	C ₂ D ₂ Cl ₄	"	340	72.2	6	
		Cl	H	Cl	HCB	"	363	79.5	7	
		OEt	H	H	HCB	"	340	74.2	7	
		OEt	H	Cl	HCB	"	333	72.3	7	
7. α -C ₆ H ₄ (OH)CONMe ₂ 8. N,N-Dimethylcarboxyamides		OEt	H	OEt	CDCl ₃	"	328	71.5	7	
		OH	H	H	CDCl ₃	"	323	71.7	7	
								51.3	8	
								$\Delta G^\ddagger_{298}$		
		2-Furan-			CDCl ₃	^1H (TLS)	289	63.2	2	
		3-Furan-			CDCl ₃	"	286	63.6	2	
		2-Thiophene-			CDCl ₃	"	274	60.7	2	
		3-Thiophene-			VC ^e	"	222	—	2	
		2-Pyrrole-			CDCl ₃	"	278	60.2	2	
		3-Pyrrole-			CDCl ₃	"	279	61.1	2	
		$\underline{RX}$								
		CH ₃ I			Water	^1H (TLS)	343	84.6	5	
		C ₆ H ₅ CH ₂ Cl			Water	"	353	87.0	5	

a. $\Delta G^\ddagger$ and $\Delta H^\ddagger$ are in kJ mol^{-1} ; $\Delta S^\ddagger$ in $\text{J mol}^{-1} \text{K}^{-1}$.

b. (TLS) = total lineshape analysis.

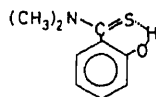
c. (T_c) = approximate value by coalescence temperature method.

d. HCB = Hexachlorobutadiene.

e. VC = Vinyl chloride.

References: 1. Fong *et al* (1978a); 2. Davis *et al* (1976); 3. Fong *et al* (1978b); 4. Spassov *et al* (1974b); 5. Lepoivre *et al* (1975); 6. Sattler and Schunack (1975); 7. Newkome and Kawato (1978); 8. Hirota and Todokoro (1974).

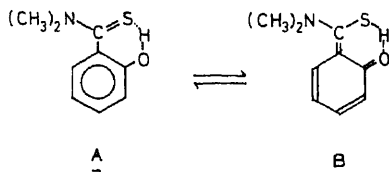
bonding, which enhances the conjugative stabilization of the transition state by localizing the π -electrons at the ring-carbonyl system (Jackman 1975). In addition, in the case of thiobenzamides, there seems to be steric destabilization of the ground state. Berg (1976) studied a series of *ortho*- and *para*-hydroxy and methoxy substituted N,N-dimethylthiobenzamides **10** and -thionaphthamides **11** using DNMR, IR and UV. The



10 (R = 2-OH)

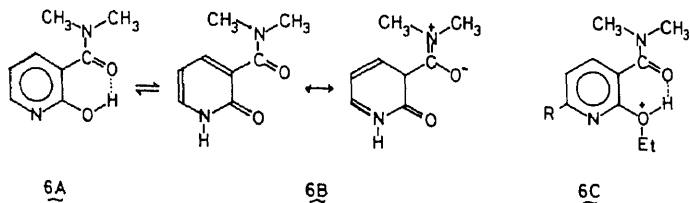
results showed comparatively weak intramolecular hydrogen bonds for the *ortho*-hydroxy derivatives indicating that in the ground state there exists a sterically induced twist around the Ar-C(S) bond, as well as around the C-N bond. In the transition state, with no steric problem, the sulphur atom can be at a location in the ring allowing formation of a stronger hydrogen bond. Thus, the stabilization of the transition state and destabilization of the ground state both contribute to lowering of the rotational barrier.

Another possibility, as pointed out by Berg (1976), involves a rapid tautomeric equilibrium involving the quinoid form **10B**. If the process is fast and reversible, the



10 (R = 2-OH)

observed rate constant for the rotation will be a weighted mean value between those of thioamide (A) and quinoid (B) forms. Though the existence of the quinoid form could not be confirmed in this case, it was shown to be the predominant form in the case of *o*-hydroxynicotinamide **6** ($R^1 = \text{OH}$, $R^2 = R^3 = \text{H}$). Newkome and Kawato (1978)

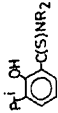
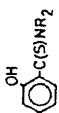


found the rotational $\Delta G^\ddagger$ was unaffected by the presence of the *o*-hydroxy group (see nicotinamides **6**, table 10). This high rotational barrier of *o*-hydroxynicotinamide was explained by assuming that the compound exists predominantly in the pyridone form **6B**, and consequently no intramolecular hydrogen bond is formed. As proof, when a trace of HCl gas was added to the solution of **6C** ($R^1 = \text{OEt}$), the rotational barrier was lowered considerably, indicating the O-protonation resulted in intramolecular hydro-

Table 10. Barriers to internal rotation in N,N-disubstituted aromatic thioamides.

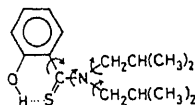
No.	Compound	Substituent: R	Solvent	Process observed	T (K)	$\Delta G_f^\ddagger$ (kJ mol ⁻¹)	Reference
10.		2-OH	DCB	C(S)-N	302.5	64.0	1
		4-OH	DMSO-d ₆	C(S)-N	343.6	73.6	1
		2-OMe	DCB	C(S)-N	440.0	93.7	1
		4-OMe	DCB	C(S)-N	335.5	71.1	1
		2-OH, 4-OMe	CDCl ₃ /C ₆ H ₅ F	C(S)-N	258.7	55.6	1
			Pyridine-d ₅	C(S)-N	298.1	63.6	1
		2-OMe, 4-OH	DCB	C(S)-N	431.2	91.6	1
			DMSO-d ₆	C(S)-N	428.9	91.6	1
		2-OMe, 4-OMe	DCB	C(S)-N	419.5	89.1	1
			DCB	C(S)-N	458.9	95.8	1
11.			DCB	C(S)-N	358.7	75.3	1
			DCB	C(S)-N	258.1	54.0	1
			DCB/C ₆ H ₅ F	C(S)-N	256.7	54.4	1
			CDCl ₃	C(S)-N	441.0	92.5	1
			DCB	C(S)-N	438.7	92.5	1
			DMSO-d ₆	C(S)-N	405.6	84.5	1
			DCB	C(S)-N			

Table 10. (Continued)

No.	Compound	Substituent: R	Solvent	Process observed	T (K)	$\Delta G_T^\ddagger$ (kJ mol ⁻¹)	Reference
12.		Me	Toluene-d ₈	C(S)-N	289	61.1	2
				Ar-C	220	49.0	2
		Et	Toluene-d ₈	C(S)-N	293	59.4	2
				Ar-C	237	53.1	2
		piperidyl	Toluene-d ₈	C(S)-N	275	56.1	2
				Ar-C	249	54.0	2
13.		Et	CH ₂ Cl ₂	C(S)-N	297	62.3	2
				Ar-C	223	46.9	2
		CH ₂ CH(CH ₃) ₂	CH ₂ Cl ₂	C(S)-N	312	65.3	2
				Ar-C	255	56.1	2
				N-CH ₂	189	36.0	2
		CH ₂ Ph	CH ₂ Cl ₂	C(S)-N	307	62.8	2
				Ar-C	263	53.6	2

DCB = *o*-DichlorobenzeneReferences: 1. Berg (1976); 2. Berg *et al* (1980).

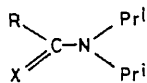
The interaction between two adjacent large alkyl substituents on the amide nitrogen produces enough of a barrier that slowing down of N-alkyl bond rotation may be observed. As a result, Bert *et al* (1980) observed three different dynamic processes in a molecule **13** through the temperature variation of its proton NMR spectra. At room temperature, the spectrum of **13** already exhibits broadened signals for isobutyl



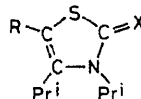
13

resonances, showing that the C–N bond rotation is slow on the NMR time scale. As the temperature is lowered, the second process causes further signal broadening and splitting of both methylene and methyl signals. The origin of this non-equivalence of geminal methylene protons has been interpreted in terms of molecular chirality due to a frozen non-coplanar conformation around the aryl–CS bond. Slowing down of N–CH₂ bond rotation was next observed at still lower temperature of 213 to 93 K (Berg *et al* 1980).

Similar interaction between two isopropyl groups was observed in N,N-diisopropylamides, in -thioamides and in analogous carbamates **14** and **15** and in 3,4-diisopropylthiazole derivatives **16** and **17**. Careful examination of their temperature dependent spectra revealed that the rotations of the isopropyl groups take place one at a time rather than by a concerted rotation of both groups (Liljefors and Sandström 1977).



14, 15 (X = O or S)



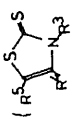
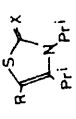
17 (X = O or S)

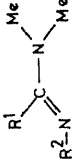
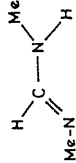
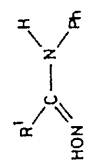
Table 11 also contains activation parameters observed in other related compounds, such as carbamates, thiocarbamates, amidines and enamines.

In view of the important role that hydrogen bonding of the amide N–H unit plays in determining the secondary and tertiary structure of proteins, it would be more interesting to investigate the effect of solvent on the C–N rotational barrier of primary and secondary amides. However, rapid relaxation due to the quadrupolar ¹⁴N nucleus causes a considerable degree of broadening of the amide N–H proton spectra so that it is difficult to conduct accurate bandshape analysis without using heteronuclear decoupling or ¹⁵N enrichment. Consequently, there have been only a small number of DNMR studies of primary amides (table 12), compared with an enormous accumulation of data on tertiary amides. Analysis of barrier heights is further complicated in the case of secondary amides when only one conformational isomer is present in a detectable proportion (Stewart and Siddall 1970) due to the ground-state energy differences.

Primary and secondary amides are excellent proton donors, as well as proton acceptors. Molecular orbital calculations indicated that the proton accepting ability of

Table 11. Barriers to internal rotation in miscellaneous amides, thioamides and related compounds.

No.	Compound	Substituent: R	Solvent	Process observed	T (K)	$\Delta G_T^\ddagger$ (kJ mol ⁻¹)	Reference
14.	RC(O)NPr ₂	H	(CD ₃) ₂ O	N-Pr ⁱ	150	32.6	1
		Me	CHFC1 ₂	N-Pr ⁱ	197	51.0	1
		MeO	CHFC1 ₂	C(O)-N		51.1	2
				N-Pr ⁱ	180	39.8	2
		MeS	CHFC1 ₂	C(O)-N		58.1	2
				N-Pr ⁱ	238	55	2
15.	RC(S)NPr ₂	Me	CHFC1 ₂	N-Pr ⁱ		57.7	1
		MeS	CHFC1 ₂	N-Pr ⁱ	265	56.9	1
				N-Pr ⁱ	219	49.8	1
16.		R ³					
		Et					
		CH ₂ Bu ^t					
		Et					
		Et					
17.		R					
		H					
		Me					
		Me					
		Me					

18.	RC(O)NMe ₂	MeO PhO <i>p</i> -NO ₂ PhO PhS <i>p</i> -NO ₂ PhS	CCl ₄ C ₆ H ₃ Br C ₆ H ₃ Br C ₆ H ₃ Br C ₆ H ₃ Br	C(O)-N C(O)-N C(O)-N C(O)-N C(O)-N	300	64.9 67.4 70.3 62.3 62.8	6 7 7 7 7
19.		CH ₂ CH ₂ CH=CH	C ₂ D ₂ Cl ₄ C ₂ D ₂ Cl ₄	C(O)-N C(O)-N		73.3 68.9	8 8
20.	Amidines 	$\frac{R^1}{H}$ $\frac{R^2}{Ph}$ Et Ph Bu ⁿ Ph Ph Ph	CDCl ₃ CH ₂ =CCl ₂ CDCl ₃ CDCl ₃		318 278 213 215 261	62.3 (¹³ C) 61.5 (¹ H) 46.0 46.0 53.6	9 9 9 9 9
21.			Neat CD ₃ NH ₂ CDCl ₃ (0.5m) CDCl ₃ (2.9m)	<i>T</i> (K) 298 298 298 298	$\Delta G_T^\ddagger$ 56.2 55.3 51.0 52.0	$\Delta H^\ddagger$ $\Delta S^\ddagger$ 39.1 -58 55.7 +1 54.1 +10 55.7 +12	10 10 10 10
22.			DMSO-d ₆		90.1 83.3	88.3 -5 88.5 14	11 11

No.	Compound	Substituents	Solvent	Rotation observed	T (K)	$\Delta G^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
23. Enamines									
		H	CCl ₄		298	54.0	57.3	11.3	12
		CN	TCE		298	74.1	69.0	-16.4	12
		H	Methanol		255	54.4	58.6	16.4	13
		MeCO	CDCl ₃		255	51.0	57.3	25	13
24.									
		R	CH ₂ Cl ₂	C=C	298	66.1	34.7	-105	14
		Me		C-N	298	54.0	57.3		14
		Et	CH ₂ Cl ₂	C=C	274	59.8			14
				C-N	257	55.2			14
		Pr ⁱ	CH ₂ Cl ₂	C=C	246	54.0			14
				C-N	250	55.2			14
			C ₆ Cl ₆	C=C	298	> 97.1	> 80		14
			CH ₂ Cl ₂	C-N	143	< 30.5	< 31.8		14
			Cl-Naph ^d	C=C	298	80.3	63.6	-56	14
			CH ₂ Cl ₂	C-N	281	60.2	63.2		14
			C ₆ H ₅ Br	C=C	298	73.2	52.3	-72	14
			CH ₂ Cl ₂	C-N	293	60.2	63.3		14
			CH ₂ Cl ₂	C=C	298	61.1	39.3	-74	14
			CH ₂ Cl ₂	C-N	247	51.0	54.0		14

a. $\Delta G^\ddagger$ and $\Delta H^\ddagger$ are in kJ mol^{-1} ; $\Delta S^\ddagger$ in $\text{J mol}^{-1} \text{K}^{-1}$.

b. $b \rightarrow a_1 + a_2$. a_1 , a_2 and b are the energy minimum conformations.

c. $a_1 \rightarrow a_2$. a_1 , a_2 and b are the same as above.

d. Cl-Naph = 1-Chloronaphthalene.

References: 1. Liden *et al* (1976); 2. Liljefors and Sandström (1977); 3. Gallo *et al* (1975); 4. Carter *et al* (1975b); 5. Liden *et al* (1974); 6. Tanny *et al* (1973); 7. Kornberg and Kost (1979); 8. Sattler and Schunack (1975); 9. Filleux *et al* (1974); 10. Halliday *et al* (1978); 11. Dondoni *et al* (1975); 12. Hobson and Reeves (1973); 13. Filleux-Blanchard *et al* (1974); 14. Osman and Shvo (1978).

moiety, and its ability to act as a proton donor is far greater (by about 11.7 kJ mol^{-1}) than that of an amide N-H bond (Johansson *et al* 1974). As a result, these amides are strongly associated *via* hydrogen bonding in practically all solutions. The activation parameters for the C-N internal rotation of primary amides should, therefore, be interpreted with such conditions in mind. As in the case of N,N-dimethylamides, alkylation of the formyl proton of formamide seems to contribute to stabilization of the transition state by localizing the amide π -system on the carbonyl group, and decreases the rotational energy barrier (*cf.* table 12). A steric factor will not play a large part in primary amides and the decrease in $\Delta G^\ddagger$ on going from formamide to acetamide is smaller accordingly. The decrease in $\Delta G^\ddagger$ from dimethylformamide (DMF) to dimethylacetamide (DMA) is 11.7 kJ mol^{-1} (neat), while that from formamide to acetamide in MPK is only 4.4 kJ mol^{-1} . Primary and secondary amides will be further discussed in connection with their intermolecular interactions in solutions in §4.2.

3.2b. *N-acylpiperidines and related systems*: The main interest in the DNMR studies on N-acyl derivatives of heterocyclic compounds, *e.g.* piperidines **25**, piperazines **26** and morpholines **27**, is related to the possibility of three types of motions that may be involved in the dynamic process; amide bond rotation, ring reversal and nitrogen inversion. This potentially complicated system, however, usually exhibits only one rate process at a temperature, since the latter two processes have relatively low barriers. The $\Delta G^\ddagger$ values for a ring reversal process in these compounds are of the order of $40\text{--}50 \text{ kJ mol}^{-1}$, (Anet and Anet 1975), and for nitrogen inversion, the barrier is

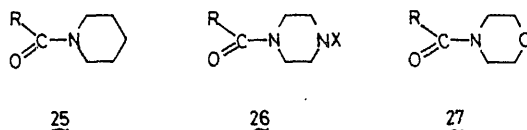


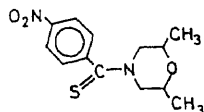
Table 12. Barriers to rotation about the C-N Bond in primary amides and thioamides^a.

Compound	Solvent (Conc.)	$\Delta G^\ddagger_{298}$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
HCONH ₂	Dyglyme (14.1 m %)	74.5	79.5	16.7	1
	MPK (9.4 m %)	74.3	77.4	11.3	1
CH ₃ CONH ₂	MPK (5.9 m %)	70.1	80.8	35.8	2
CFH ₂ CONH ₂	DMF	69.1	64.0	-17.2	3
CF ₂ HCONH ₂	DMF	76.4	78.3	6.3	3
CF ₃ CONH ₂	Dioxane (16 m %)	74.0	74.5	2.1	4
	MPK (18 m %)	73.6	74.5	3.3	4
CH(CH ₃) ₂ CONH ₂	DMF	69.0 (335 K)			5
C(CH ₃) ₃ CONH ₂	DMF	67.4 (323 K)			5
C ₆ H ₅ CONH ₂	DMF	66.1 (325 K)			5
HCSNH ₂	DMF	≥ 85 ($> 391 \text{ K}$)			5
CH ₃ CSNH ₂	DMF	> 89 ($> 404 \text{ K}$)			5
CH(CH ₃) ₂ CSNH ₂	Ether	82.4 (388 K)			5
C(CH ₃) ₃ CSNH ₂	Ether	82.0 (396 K)			5
C ₆ H ₅ CSNH ₂	DMF-d ₇	79.5 (363 K)			5

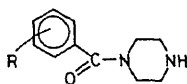
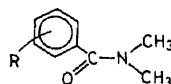
a. $\Delta G^\ddagger$ and $\Delta H^\ddagger$ are in kJ mol^{-1} ; $\Delta S^\ddagger$ in $\text{J mol}^{-1} \text{ K}^{-1}$.

References: 1. Drakenberg and Forsén (1970); 2. Umamoto and Ouchi (1981);

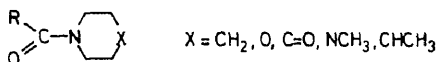
estimated to be even smaller (Anet and Yavari 1977a, b), though ^{13}C NMR is not capable of distinguishing ring reversal from nitrogen inversion and some ambiguity always remains (Hirsch *et al* 1975). Slowing down of the ring reversal process has been directly observed at -80 to -110°C in a derivative of thiobenzmorpholide **28**, with an upper limit of $\Delta G^\ddagger$ being estimated to be about 33 kJ mol^{-1} (Berg 1977).

**28**

The values of reported activation free energies $\Delta G^\ddagger$, summarized in table 1, are mostly in the range of 55 – 70 kJ mol^{-1} , indicating that the dynamic process observed is that of the amide bond rotation, rather than ring reversal or nitrogen inversion processes. Moreover, a linear correlation is found between the $\Delta G^\ddagger$ of substituted phenyl piperazines **29** and those of substituted benzamies **30** showing that the mechanism of the dynamic process is similar and not much influenced by whether the N-alkyl groups are open chains or components of one alicyclic ring (Ciureanu *et al* 1981).

**29****30**

Effects of substituents at the 4-position in the six-membered ring on the rotation barriers in **31** were studied by Hirsch *et al* (1975), Hirsch (1979). As seen from the results listed in table 13, the rotational barriers of benzoyl derivatives increase in the order, 4-piperidone ($\text{X} = \text{C}=\text{O}$) < morpholide ($\text{X} = \text{O}$) < 4-methylpiperazine ($\text{X} = \text{NCH}_3$) < piperidine ($\text{X} = \text{CH}_2$).

**31**

The question of whether the N-acyl group is coplanar (I) with or perpendicular to the virtual (*i.e.* ring reversal- and inversion-averaged) plane of piperidyl ring in the ground state has been studied by Lunazzi *et al* (1980a). The ^{13}C NMR spectra of **31** effectively distinguish (I) from (II) provided that the spectra are taken at temper-



Table 13. Barriers to internal rotation about the C-N bond in N-acylpiperidines and related compounds^a.

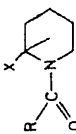
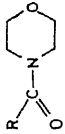
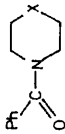
No.	Compound	R	Substituent	X	Solvent	Nucleus observed	$\Delta G^\ddagger(T)$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
25.	Piperidines 	Ph	—	—	CDCl ₃	α - ¹ H α - ¹³ C β - ¹³ C ¹³ C	62.0 (292) 62.5 (316) 61.7 (289) 61.5 (309)			1 1 1 2
		Ph	—	—	DCB	α - ¹³ C	59.0 (281)			3
		OMe	—	—	CHCl ₂	α - ¹³ C	49.7 (223)			1
		Me	2-Me	—	Toluene-d ₈	¹ H(MeCO) ¹ H(2-Me)	62.9 (279) 63.1 (291)			4 4
		Me	4-Me	—	CDCl ₃	α - ¹ H	71.4 (343)			5
		Me	4-Ph	—	Toluene-d ₈	α - ¹ H	69.8 (357)			4
		Ph	2,4-Me ₂ (cis)	—	CDCl ₃	α - ¹ H	55.1 (263)			1
		<i>p</i> -MePh <i>p</i> -NO ₂ Ph	—	—	—	¹³ C ¹³ C	59.2 (299) 64.1 (323)			2 2
		<i>p</i> -OMePh PhCH ₂	—	—	DCB		62.3 (298) 54.4 (256)			3 3
		Me	—	—	DCB		69.5 (345)			3
27.	Morpholides 	Ph	—	—	CHCl ₂	β - ¹ H α - ¹ H ¹³ C ¹³ C ¹³ C	69.0 (305) 69.5 (315) 59.6 (300) 58.9 (298) 62.9 (316)			6 6 2 2 2
31.		Ph	—	—	CDCl ₃	α - ¹ H α - ¹³ C α - ¹³ C α - ¹³ C β - ¹³ C α - ¹ H α - ¹³ C	62.0 (292) 62.5 (316) 60.2 (305) 61.3 (310) 61.3 (284) 57.7 (273) 59.9 (303)			1 1 1 1 1 1 1

Table 13. (Continued)

No.	Compound	R	Substituent	X	Solvent	Nucleus observed	$\Delta G^\ddagger$ (T) $\Delta H^\ddagger$ $\Delta S^\ddagger$	Reference
32.		Me Ph Bu ^t			CDCl ₃ CHF ₂ Cl CHF ₂ Cl	Average ^c Average Average	57.7 (266-291) 50.6 (243-256) 51.5 (239-255)	7 7 7
33.		Me Ph			CHF ₂ Cl/CHFCl ₂ CHF ₂ Cl/CHFCl ₂	Average Average	28.0 (140) 28.0 (140)	7 7
	Piperidylamidines							
34.		Me Ph			CS ₂ CHF ₂ Cl		45.6 (228) 44.4 (218)	7 7
35.		Me Ph			CHF ₂ Cl CHF ₂ Cl		33.5 (177) 37.2 (195)	7 7
36.	3-Piperidonides	Ph Me OMe OEt			CDCl ₃ (CD ₃) ₂ CO CDCl ₃ CDCl ₃ CDCl ₃ CDCl ₃	Average Average 1 ^s C (amide) 1 ³ C (ketone) 1 ³ C-2 1 ³ C (ketone) 1 ³ C (amide) 1 ³ C (amide) 1 ³ C-6 1 ³ C (ketone) 1 ³ C-2 1 ³ C (ketone) 1 ³ C-2 1 ³ C (ketone) 1 ³ C-2 1 ³ C (amide)	66.6 (253-305) 65.2 (259-290) 77.5 (309) 77.8 (317) 67.3 (273) 66.6 (268) 67.4 (273) 65.9 (267) 66.8 (267) 66.9 (267) 67.3 (276) 66.2 (264) 66.6 (271) 66.7 (270)	8 8 8 8 8 8 8 8 8 8 8 8 8 8 8
		OCH ₂ Ph			CDCl ₃			

			$\Delta G_{298}^\ddagger$	
37.		Ph <i>p</i> -ClPh <i>p</i> -MeOPh <i>p</i> -NO ₂ Ph <i>p</i> -NO ₂ Ph 4-pyridyl Ph <i>p</i> -ClPh Pyridine-d ₅ <i>p</i> -MeOPh <i>p</i> -NO ₂ Ph 4-pyridyl Pyridine-d ₅	61.5 60.8 57.6 63.5 66.3 72.6 73.5 68.2 76.2 77.3	2.1 -3.1 -0.2 -3.1 -0.2 -3.0 1.6 -0.3 0.7 -2.0
		(CD ₃) ₂ CO (CD ₃) ₂ CO (CD ₃) ₂ CO (CD ₃) ₂ CO (CD ₃) ₂ CO CDCl ₃ Pyridine-d ₅ Pyridine-d ₅ Pyridine-d ₅ Pyridine-d ₅ Pyridine-d ₅	62.1 59.9 57.6 62.6 66.2 71.8 74.0 68.1 76.4 76.7	9 9 9 9 9 9 9 9 9 9

38.	Thioperidides 	PhCH ₂ PhCH ₂ <i>p</i> -NO ₂ Ph <i>m</i> -NO ₂ Ph Ph <i>p</i> -ClPh <i>p</i> -MeOPh <i>m</i> -NO ₂ PhCH=CH <i>p</i> -ClPhCH=CH PhCH=CH <i>p</i> -MeOPhCH=CH CH=CH <i>p</i> -NO ₂ Ph Ph <i>p</i> -MeOPh	¹ H ¹ H ¹ H ¹ H ¹³ C ¹ H ¹ H ¹ H ¹ H ¹ H ¹³ C ¹ H ¹³ C ¹³ C	80.4 (389) 80.8 (388) 74.9 (362) 73.2 (356) 72.0 (354) 72.8 (353) 71.5 (347) 66.9 (324) 67.2 (325) 65.8 (319) 65.7 (318) 64.5 (313) 64.0 (311) 72.0 (348) 69.0 (338) 63.6 (312)	10 3 3 3 10 3 3 3 10 10 10 10 10 3 3 3
39.	Thiomorpholides 	<i>p</i> -NO ₂ Ph Ph <i>p</i> -MeOPh	¹³ C ¹³ C ¹³ C	72.0 (348) 69.0 (338) 63.6 (312)	3 3 3
40.	N-Acylpyrrole 		¹ H-2,5	54.0 (257)	11

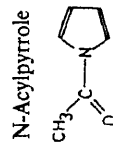
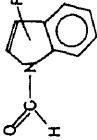
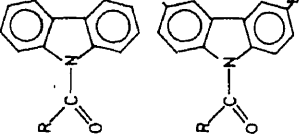


Table 13. (Continued)

No.	Compound	R	Substituent	X	Solvent	Nucleus observed	$\Delta G^\#(T)$	$\Delta H^\#$	$\Delta S^\#$	Reference
41.	N-Acylindoles 	H 3-Me 2,3-Me ₂			CDCl ₃ CDCl ₃ CDCl ₃	¹ H(CHO) ¹ H(CHO) ¹ H(CHO)	61.5 (288) 63.1 (Z → E) 68.1 (318) 70.0 (Z → E) 60.0 (283) 66.1 (Z → E)	(E → Z) (E → Z) (E → Z)		11 11 11 11 11 11
42.	N-Acylcarbazoles 	H Me Et Pr ⁱ Bu ^t CF ₃ Ph H Me			THF C ₂ Cl ₄ THF CHFCI ₂ CHFCI ₂ CHFCI ₂ CHFCI ₂ CHFCI ₂ CHFCI ₂ CHFCI ₂ THF THF	¹ H-1,8 ¹³ C (Av.) ^c ¹ H-1,8 ¹³ C (Av.) ¹³ C (Av.) ¹³ C (Av.) ¹³ C (Av.) ¹³ C (Av.) ¹³ C (Av.) ¹³ C (Av.) ¹ H-1,8 ¹ H-1,8	62.0 (298) 62.8 45.5 (223) 39.6 40.2 41.0 Undetected 38.1 29.7 62.8 (300) 44.0 (213)			12 13 12 13 13 13 13 13 13 12 12

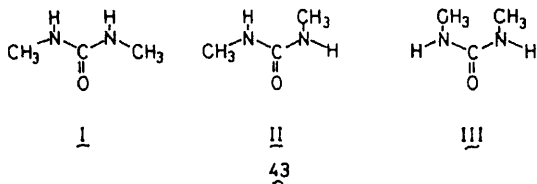
a. $\Delta G^\#$ and $\Delta H^\#$ are in kJ mol^{-1} ; $\Delta S^\#$ in $\text{J mol}^{-1} \text{K}^{-1}$; T in Kelvin.References: 1. Hirsch *et al* (1975); 2. Buhleier *et al* (1979); 3. Piccinni-Leopardi *et al* (1977); 4. Fraser and Grindley (1974); 5. Johnson (1968); 6. LeCam and Sandström (1971); 7. Lunazzi *et al* (1980a); 8. Hirsch (1979); 9. Benassi *et al* (1981); 10. Ciureanu *et al* (1981); 11. Elguero *et al* (1974); 12. Elguero *et al* (1975); 13. Cipiciani *et al* (1979).

low enough that rotation about the C-N bond is slow on the NMR time scale. In the planar conformation (I), the 2- and 6-methyl carbons, as well as C-2 and C-6 are non-equivalent, whereas in the perpendicular conformation (II), only the 2- and 6-methyls remain non-equivalent, that is, the equatorial and axial methyls never become equivalent despite rapid ring reversal and nitrogen inversion (Lunazzi *et al* 1980a). The ^{13}C spectra of the series of compounds **32** observed at various temperatures show separate peaks for C-2 and C-6 (also for C-3 and C-5) of the piperidyl ring as well as for 2- and 6-methyl carbons, suggesting the planar (I) ground state conformation for the rotational process. In addition, the decrease of $\Delta G^\ddagger$ from 2,6-dimethyl **32** to 2,2,6,6-tetramethyl **33** derivatives, and also from $\text{R}=\text{Me}$ to $\text{R}=\text{Bu}^t$, strongly indicates the steric destabilization of the planar ground state, not that of the transition state. Interestingly, however, they found the heavily substituted piperidyl amidines to be in the perpendicular form (II) in their ground state. While, 2,6-dimethylpiperidylamidines **34** with $\text{R}=\text{Me}$ and Ph were planar (I), the tetramethyl derivatives **35** were perpendicular (II) in their ground states. Thus the conjugational stabilization by phenyl substitution is effective in the direction of the transition state in compounds **34**, lowering the C-N rotational barrier, whereas in compounds **35**, the same stabilization is more effective in the direction of the ground state and increases the barrier instead (*cf.* table 13).

Internal rotation in N-acylpyrroles **40**, -indoles **41** and -carbazoles **42** was studied and the results are included in table 13.

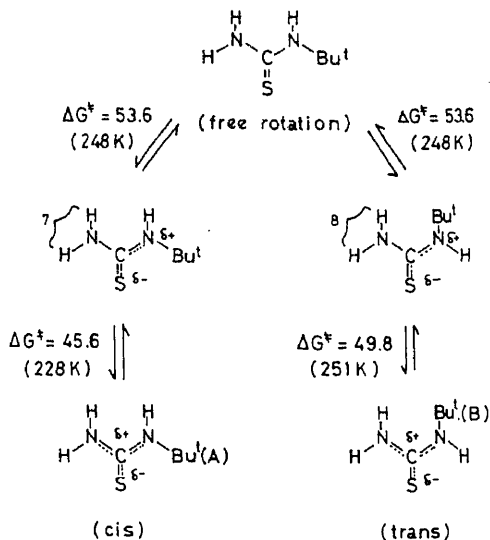
2c. *Urea and thiourea*: The C-N bond of urea and thiourea is known to possess appreciable double bond character, as in the case of amides, and thus exhibits hindered internal rotation. Because of the competitive conjugation between the two amino groups with the carbonyl, however, the rotational barriers are always lower in ureas and thioureas than in corresponding amides. Moreover, larger steric hindrance is to be expected among the amino substituents, leading to destabilization of the planar ground state and to a further decrease in the rotational barrier.

Three isomers are possible for N,N'-dimethylurea **43**. From steric grounds, a



conformation of type III seems unfavourable, and such is the result found by Sullivan and Price (1975) in the corresponding thiourea in pyridine- d_5 . However, in the solid state, an x-ray study has indicated that type III is the conformation preferred in spite of marked torsion of the skeleton (Lepore *et al* 1976). A pronounced solvent dependence of the isomer ratio has also been reported for 1-methylthiourea (Tomba *et al* 1969; Walter and Reuss 1971). Thus the isomer ratios will vary dependent on the relative stability of their ground states, and the study of the dynamic processes could become quite complex due to the simultaneous existence of multiple conformational isomers.

The equilibria among the isomers of 1-t-butylthiourea **44** may be described as



44

The temperature variation of the ^1H NMR spectra of **44** correspondent to the scheme above has been reported by Sullivan and Price (1975) and is illustrated in figure 5. At 210 K, the spectrum is comprised of six resonance lines from each of the three N-H protons of the two isomers, and the two methyl peaks. As the temperature is increased, the amino group of the *cis* isomer starts to rotate at 228 K and the lines due to protons 3 and 4 coalesce; protons 1 and 2 coalesce next at 251 K; and then peaks due to the NHBu^t group coalesce at 248 K. Table 14 summarized the free energy of activation for the rotation in ureas and thioureas.

It is noted in table 14 that the rotational $\Delta G^\ddagger$ for the NHCH_3 group in 1-methylthiourea is about 10 kJ mol^{-1} larger than the $\Delta G^\ddagger$ value of the same group in N,N'-dimethylthiourea. As Anet and Ghiaci (1979a) pointed out, the rotation of the first amino group is less hindered than the second group rotation, since with one group rotating, the cross conjugation is hindered and the remaining C-N bond has a double bond character similar to that of amides. The activation energies $\Delta G^\ddagger$ of the substituted amino groups are thus largely dependent on whether or not the group is the first to rotate.

Three factors are considered to affect the energy barrier to C-N bond rotation in ureas; (i) the extent of electron delocalization along the C-N bond, (ii) steric destabilization of the ground state by bulky N-substituents, and (iii) stabilization of the ground state by intermolecular hydrogen bonding. A steric effect is particularly evident on the $\Delta G^\ddagger$ values observed in the various N-alkyl and -aryl substituted ureas and thioureas listed in table 14. Introduction of a second substituent onto mono-substituted urea increases steric repulsion between the substituents and decreases the barrier considerably. Complete substitution of all four hydrogens on urea or thiourea with methyl groups produces such severe steric repulsions that no delocalization of electrons on nitrogen seems to occur and, as a result, the C-N bonds have rotational barriers that are close to those of the single bond in amines. The barriers in tetramethyl-

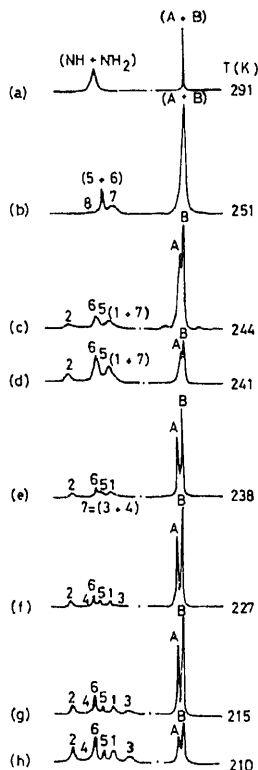


Figure 5. NMR spectra of 1-*t*-butylthiourea (**44**) in pyridine- d_5 at 60 MHz. Reproduced from Sullivan and Price (1975) by permission of Heyden and Son Ltd.

2d. Amines: Aromatic amines exhibit partial double bond character for the C–N bond, because of conjugation of the nitrogen lone pair with the aromatic moiety as illustrated by the resonance structure **B** of *N*-methylaniline **47**. The barriers are, however, considerably lower than those found in amides and thioamides. Lunazzi *et al* (1979) employed ^{13}C DNMR bandshape analysis to obtain the activation parameters of *N*-methylaniline **47** in acetone. At temperatures between 160 K and 147 K, they observed the slowing down of the C–N bond rotation (figure 6) and obtained a $\Delta G^\ddagger$ of 10.3 kJ mol^{-1} .

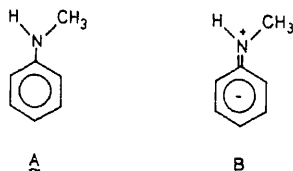


Table 14. Barriers to internal rotation about the C-N bonds in ureas and thioureas^a.

No.	Compound	Substituents	Solvent ^b	Rotating bond	T (K)	$\Delta G_T^\ddagger$	Reference
	$ \begin{array}{c} R^1 \quad R^3 \\ \quad \\ N^1 \quad N^3 \\ \diagup \quad \diagdown \\ C^2 \\ \\ O \end{array} $						
43.	Urea	R^1 H R^3 CH ₃					
				(One isomer predominant)			1
				C ² -N ¹ , N ³	220	47.2	2
44.		H H H H	DMF/DMSO	C ² -N ¹	220	~ 41	1
		H H H H	CH ₃ OH	C ² -N ³ (c → t) ^c	253	55.2	1
				C ² -N ³ (t → c)	51.4	51.4	1
		H H CH ₃ CH ₃	(CD ₃) ₂ CO	C ² -N ¹	211	40.9	1
		H H Et Et	(CD ₃) ₂ CO	C ² -N ³	211	44.5	1
		H H CH ₃ CH ₃	(CD ₃) ₂ CO	C ² -N ¹	205	43	1
		H H CH ₃ CH ₃	(CD ₃) ₂ CO	C ² -N ³	205	39.7	1
		H H CH ₃ CH ₃	(CD ₃) ₂ CO	C ² -N ¹	< 37	< 37	1
		H H CH ₃ CH ₃	(CD ₃) ₂ CO	C ² -N ³	< 37	< 37	1
		H Et Me Me	CHFCI ₂ /Ftol	C ² -N ¹	298	40.5	3
		Me Me Me Me	CHFCI ₂ /CHF ₂ Cl	C ² -N ¹ , N ³	135(¹³ C) (¹ H)	26.4 26.8	4 4
			CHFCI ₂ /CDCl ₃ / (CD ₃) ₂ CO		(T _{1ρ})	25.5	7
		Me Et Et Et	CD ₂ Cl ₂	C ² -N ¹ , N ³		< 33.4	1
		Et Et Et Et	CD ₂ Cl ₂	C ² -N ¹ , N ³		< 33.4	1
45.	Thiourea	H H H Bu ^t	Py-d ₅	C ² -N ³	247	53.1	5
				C ² -N ¹ (t)	251	49.8	5
				C ² -N ¹ (c)	228	45.6	5
	$ \begin{array}{c} R^1 \quad R^3 \\ \quad \\ N^1 \quad N^3 \\ \diagup \quad \diagdown \\ C^2 \\ \\ S \end{array} $						

46.

H	H	H	H	Py-d ₅	C ² -N ¹ ,N ³	57.2	5
H	H	H	CH ₃	Py-d ₅	C ² -N ³	294	5
					C ² -N ¹ (t)	273	5
					C ² -N ¹ (c)	223	5
					C ² -N ³	283	5
H	H	H	Et	Py-d ₅	C ² -N ¹ (t)	270	5
					C ² -N ¹ (c)	230	5
H	H	H	Ph	(CD ₃) ₂ CO	C ² -N ³	253	6
H	H	H	Me	CH ₃ OH	C ² -N ³	268	6
				(CD ₃) ₂ CO	C ² -N ¹	239	6
H	Me	H	Me	Py-d ₅	C ² -N ¹ ,N ³	53.1	5
H	Me	H	Bu ^t	Py-d ₅		48.9	5
H	Et	H	Et	Py-d ₅	C ² -N ¹ ,N ³	48.9	5
H	Pr ⁱ	H	Pr ⁱ	Py-d ₅	C ² -N ¹ ,N ³	48.1	5
H	Bu ^t	H	Bu ^t	CH ₂ Cl ₂	C ² -N ¹ ,N ³	46.4	6
Me	Me	Me	Me	CHClCl ₂ /CHF ₂ Cl	C ² -N ¹ ,N ³	26.4	4

a. $\Delta G^\ddagger$ in kJ mol⁻¹.b. Py-d₅ = pyridine-d₅; Ftol = 3-fluorotoluene.c. c = Me-C=O *cis*; t = Me-C=O *trans*.References: 1. Martin *et al* (1980); 2. Stilbs and Forsén (1971); 3. Stilbs (1971); 4. Anet and Ghiaci (1979a); 5. Sullivan and Price (1975); 6. Filleux-Blanchard and Durand (1972); 7. Stilbs and Mossley (1978).

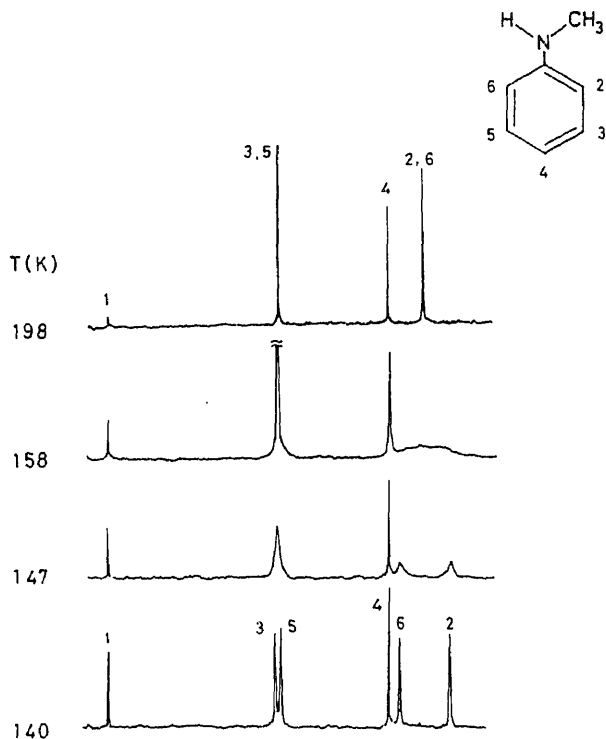
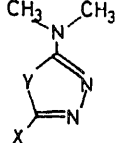


Figure 6. ^{13}C NMR spectra of N-methylaniline in Me_2O . Reproduced from Lunazzi *et al* (1979) by permission of Pergamon Press Ltd, Oxford.

atom. The problem was studied by Barbieri *et al* (1979) employing *ab initio* molecular orbital theory with the STO-3G minimal basis set. The results on N,N-dimethylaniline showed that the most stable conformation corresponding to the angle of rotation $\theta = 0$ is that having a nitrogen which is pyramidal, with ϕ , the dihedral angle between the CNC plane and the plane of the benzene ring, equal to 22° . The inversion barrier at $\phi = 0$, however, is rather small, about 3 kJ mol^{-1} , and the pyramidal nitrogen may be considered as rapidly inverting to produce an effectively all-planar ground state.

As is evident from the resonance structure **B** above, the presence of electron-withdrawing groups in the aromatic π -system enhances the delocalization of the electrons of nitrogen and thus increases the energy barrier for internal rotation about the C-N bond. In this context, a number of aromatic and heteroaromatic N,N-dimethylamines have been treated using CNDO/2 by Barbieri *et al* (1979), who found that the experimental free energy of activation ($\Delta G^\ddagger$) is nicely correlated with π -bond order for the C-N bond for the planar conformation, as shown in figure 7.

Linear correlations between the activation-free energy $\Delta G^\ddagger$ and the Hammett σ^- values of the substituents were also found by Liljefors (1974) in substituted dimethylaminoazoles **50**. When X is a nitro group, the barrier ($\Delta G^\ddagger$) is increased by about 12.2 kJ mol^{-1} for oxadiazole ($\text{Y} = \text{O}$) and 15.5 kJ mol^{-1} for thiadiazole ($\text{Y} = \text{S}$)



50 ($Y = O \text{ or } S$)

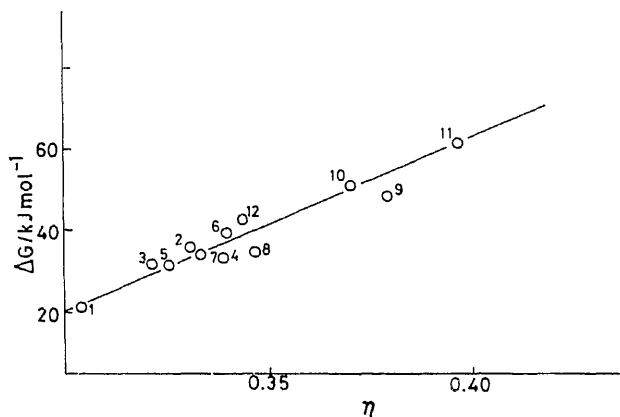


Figure 7. Correlation of the experimental free energies of activation ($\Delta G^\ddagger$) for the rotation of the dimethylamino-group in a number of aromatic and heteroaromatic systems as a function of the π -bond order η for the C–N bond calculated by CNDO/2. Reproduced from Barbieri *et al* (1979) by permission of Royal Society of Chemistry.

The presence of hetero-atoms such as N, O and S in the ring system seems to increase the rotational barrier of the amino group. This is likely due to the possibility of structures such as;



participating in the resonance. The stabilization of the planar C–N group by these resonance structures may be understood on the basis of the greater electronegativity of nitrogen and sulphur as compared with carbon.

Other heteroaromatic ring systems that have attracted attention because of their biological importance are N,N-dimethylamino substituted pyrimidine and purine derivatives. Riand *et al* (1979) studied the influence of the substituents on the restricted rotation of the dimethylamino group in 4-(N,N-dimethylamino)pyrimidine **52**, where



Table 15. Barriers to internal rotation in aromatic amines^a.

[illegible]

51.		H	CHClF ₂	150	32.2	4
		Br	CHClF ₂	151	32.2	4
		NO ₂	CHClF ₂	242	51.9	4
			Py/CD ₂ Cl ₂	233.0	49.0	3
			Py/CD ₂ Cl ₂	248.4	53.1	3
					43.9	-22
					43.9	-38

52.		$\underline{R^2}$	$\underline{R^5}$	$\underline{R^6}$		
		H	H	H	247 (¹ H)	53.5
					250 (¹³ C)	54.0
					240.2	49.8
					230.2	38.5
					268.2	58.6
					266.2	57.3
					241	51.4
					151	32
					253	51.9
					232	49.4 (4-NMe ₂)
					200	43.5 (2-NMe ₂)
					222	47.3 (4-NMe ₂)
					276	61.4
					283	62.5
					243	52.8
					230	52.7
					231	53.1
					190	52.3
					<183	
						52
						52.3
						45
						49
						46
						4
						-21
						54
						12
						-8
						-8
						-21
						50
						55
						-33
						41.6
						-48
						43.5
						-42
						23.3
						-153

Table 15. (Continued)

No.	Compound	Substituent X	Solvent ^b	T (K)	$\Delta G_T^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
53.			CDCl_3	283	62.3		31.4	7
			CD_3CN	270	61.1		- 2	7
			CD_3OD	278	63.2		1	7
			SO_2	234	53.1		-34	7
			CDCl_3	310	69.0		2	7
			CD_3CN	295	67.8		18	7
54.			$\text{D}_2\text{O}/\text{DCI}$	301	62.8	52.7	34	8

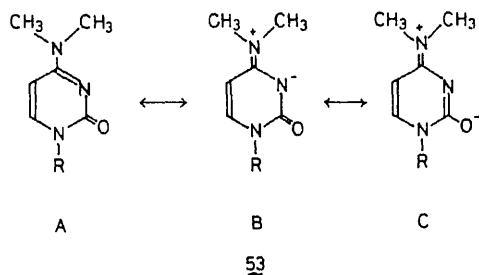
a. $\Delta G^\ddagger$ and $\Delta H^\ddagger$ are in kJ mol^{-1} ; ΔS in $\text{J mol}^{-1} \text{K}^{-1}$.

b. Py = pyridine.

References: 1. Lunazzi *et al* (1979); 2. Lunazzi *et al* (1980b); 3. Liljefors (1974); 4. Forlani *et al* (1977); 5. Riand *et al* (1979); 6. Wells (1982); 7. Shoup *et al* (1972a); 8. Pitner *et al* (1975); 9. Katritzky and Tiddy (1969).

the substituents R^2 , R^5 and R^6 are combinations of H, Me, Cl, NO_2 and NMe_2 . Similarly in the case of the benzene series, the rotational barrier is found to increase with increasing electron-withdrawing power of the substituents. The $\Delta G_c^\ddagger$ values thus increase in the order of substituents in the 2-position: $\text{NMe}_2 < \text{Me}, \text{H} < \text{Cl}$.

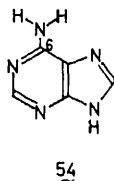
In the above system **52**, differences of 2–4 kJ mol^{-1} are observed between the $\Delta G_c^\ddagger$ values measured in CD_3OD and in CHCl_3 solutions, with the CHCl_3 solution values being lower. Stabilization of polar resonance forms in polar CD_3OD will reasonably account for this degree of solvent dependence of the rotational barriers. A similar solvent dependence has also been observed in N,N-dimethylcytosines **53** (Shoup *et al* 1972a, b). In the case of cytosine, delocalization of the amino nitrogen lone pair is



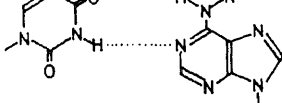
extended to the ring carbonyl group through conjugation. Consequently, the C– NMe_2 rotational barrier is still higher than in pyrimidines and is closer to the barriers found in amides.

These cytosine derivatives exhibited rotational barriers ($\Delta G_c^\ddagger$) in solvents decreasing in the order $\text{CD}_3\text{OD} > \text{CDCl}_3 > \text{CD}_3\text{CN} \gg \text{SO}_2$. Shoup *et al* (1972a) suggested that in addition to the polarity of the solvent, hydrogen bonding of the solvent to the $\text{C}=\text{O}$ group plays a role in stabilizing the resonance form C and thus increasing the double bond character of the C– NMe_2 bond. The presence of such hydrogen bonding is confirmed by the IR study. While chloroform is capable of donating a proton to form a weak hydrogen bond with carbonyl, the more polar acetonitrile is not and, therefore, is less stabilizing. When the compound **53** had a sugar moiety as the substituent R, a fairly high rotational barrier was found. Hydrogen-bonding with solvent was denied in this case on the basis of IR results. The electron-withdrawing ability of the sugar moiety is said to be responsible for this high barrier.

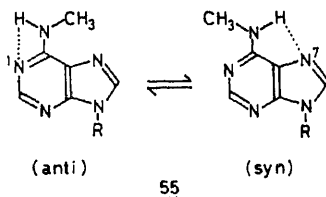
Another example of amino group rotation in nucleic acid bases is found in adenine derivatives **54**. N(6)-alkylated adenine derivatives occur as minor constituents of



nucleic acids (Davidson 1972). X-ray data show that all mono N⁶-substituted adenines

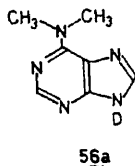


This *syn-anti* conformational problem was investigated by Dodin *et al* (1979). From IR results, both *anti*- and *syn*-rotamers are present for mono-N(6)-methyladenine **55** in chloroform. It is conceivable and also in agreement with the IR results that exocyclic

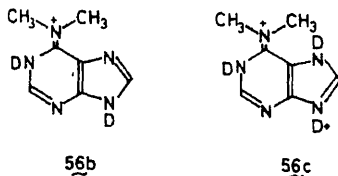


N-H...N(1) and N-H...N(7) hydrogen bonds have similar energies and, consequently, the contribution from the steric hindrance plays a determining role in this case. When the solvent is changed from chloroform to acetonitrile, the intra-molecular hydrogen bonds are observed to be destroyed by the solvent, leaving only the steric effect of the methyl group. The *syn* form thus becomes even more predominant in acetonitrile than in chloroform.

The internal rotation around the C-NMe₂ bond in N,N-dimethyladenine **56a** was investigated by Pitner *et al* (1975) and was found to be quite rapid at room temperature



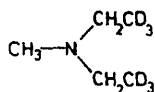
in neutral D₂O and in DMSO, so that only a single sharp methyl resonance signal was observed. When DCl was added to the D₂O solution to decrease its pD value, the methyl signal started to broaden showing that the rate of rotation had decreased, presumably due to the contributions of resonance forms such as **56b** and **56c**. The barrier to internal rotation seems to increase with increasing acidity of the aqueous solution so that it increases in the order; DM⁶A(**56a**) < DM⁶A·D⁺(**56b**)



< DM⁶A·D₂⁺(**56c**). The observed activation parameters are listed in table 15, together with those of related systems.

Carbon-nitrogen single bonds in alkylamines usually have a rotational barrier comparable to that of C–C single bonds. What is different about the C–N bond is that, in addition to bond rotation, there is a possibility of an atomic inversion process associated with the sp^3 hybridized nitrogen. In simple alkylamines, the potential barrier to nitrogen inversion is generally observed to be significantly higher than that to C–N bond rotation. However, in some substituted alkylamines, the rotational barrier is sterically increased and may become very similar in magnitude to the barrier for the nitrogen inversion. Such systems will present an interesting dynamic process where rotation and nitrogen inversion may take place concurrently.

Bushweller *et al* (1974b, 1975, 1977, 1982) Reny *et al* (1975) have made an extensive investigation of the stereodynamics of a series of simple alkylamines by means of total bandshape analysis. In partially deuterated diethylmethylamine **61**, they observed

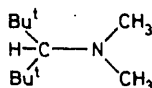


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'decoalescence' of methylene resonances at low temperatures (figure 8) consistent with slowing first of nitrogen inversion (180 to 150 K) and then of N–CH₂ bond rotation (below 150 K). Complete ¹H DNMR bandshape analysis, with the aid of empirical force-field calculations, yielded activation parameters for both of these processes (see table 16). Below 150 K, the rate constant k_i for inversion becomes sufficiently small, so that the inversion process no longer contributes to the bandshape. For accurate simulations of the N–CH₂ spectra below 150 K, it was necessary to consider three families of rotamers as illustrated in figure 9. Within a family, the conformational exchange is very rapid and DNMR-invisible, while the molecule also undergoes higher barrier inter-family exchange process *via* N–CH₂ rotation, which is DNMR-visible (Bushweller *et al* 1982).

When nitrogen has an electronegative substituent bonded directly to it, the barrier to nitrogen inversion becomes greater than that for isolated rotation; then the lower barrier process, that is rotation, takes place exclusively. This is the case found in the N-chloro- and N-bromo-amines listed in table 16 (Bushweller *et al* 1975).

An unusually large barrier to rotation is found in **60**. According to Berger and Hobbs (1978), the N-methylgroups are likely to be coplanar (or nearly coplanar) with sp^2 -hybridized nitrogen, due to the extreme crowding of the ground state.



60

3.3 Phosphorous-nitrogen bond

Although many studies on the rotation about bonds connecting a phosphorus atom have

Table 16. Barriers to rotation about the C-N bond in alkyl amines^a.

No. Compound	Substituent	Solvent	T (K)	Rate process ^b	$\Delta G_f^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
57.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{N}-\text{R}^2 \\ \\ \text{CH}_3 \end{array}$ R ¹ CD ₃ R ² CH ₂ CD ₃	CBrF ₃	145	Rot	30.5	36.0	33	1
58.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{N}-\text{R}^2 \\ \\ \text{CH}_3 \end{array}$ CH ₃ CH ₃ CH ₃ CH ₃ CH ₃ CH ₂ Ph	CH ₂ CHCl CH ₂ CHCl CH ₂ CHCl CH ₂ CHCl	120 120 120 131	Rot Rot Rot Rot	25.9 25.9 25.9 26.8	25.9 25.9 25.9	0 0 0	1 1 1 1
	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{N}-\text{R}^2 \\ \\ \text{CH}_3 \end{array}$ CH ₃ CD ₂ CD ₃ CH ₃ CD ₃ CD(CD ₃) ₂	CBrF ₃ CBrF ₃ CBrF ₃	131 116 116	Inv Rot Rot	26.4 29.7 25.1	35.6 26.8	38 17	1 1 1
	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{N}-\text{R}^2 \\ \\ \text{CH}_3 \end{array}$ Cl CH ₂ CD ₃	CBrF ₃	107 164 193	Inv Rot Inv	23.0 37.2 40.6	22.2 40.2	-8 17	1 2 2
	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{N}-\text{R}^2 \\ \\ \text{CH}_3 \end{array}$ Cl CH ₂ Ph	CD ₂ Cl ₂ /CF ₂ CFCI	151 189	Rot Inv	45.2 34.7	21 41.0	21 38	2 2
	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{N}-\text{R}^2 \\ \\ \text{CH}_3 \end{array}$ Cl CH ₃	CF ₂ CFCI	158	Rot	36.8	36.8	0	2
	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{N}-\text{R}^2 \\ \\ \text{CH}_3 \end{array}$ Br CH ₃	CF ₂ CFCI	152	Rot	35.6	36.8	8	2
	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{N}-\text{R}^2 \\ \\ \text{CH}_3 \end{array}$ Cl Cl	CH ₂ CHCl	184	Rot	40.6	43.9	17	2
59.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{N}-\text{R}^2 \\ \\ \text{D} \end{array}$ CD ₃ CH ₂ CD ₃	CBrF ₃	152 115	Inv Rot	31.4 23.4	34.7 22.2	23 -13	3 3

60.	$ \begin{array}{c} \text{Bu}^t \\ \\ \text{C} - \text{N} \\ / \quad \backslash \\ \text{Bu}^t \quad \text{CH}_3 \\ \quad \\ \text{H} \quad \text{CH}_3 \end{array} $	Pyridine-d ₅	335	Rot	77.4	4
61.	$ \begin{array}{c} \text{CH}_3 - \text{N} \\ / \quad \backslash \\ \text{CH}_2\text{CH}_3 \quad \text{CH}_2\text{CH}_3 \end{array} $	CBrF ₃	160 120	Inv Rot	33.1 24.7 (GG → AG) ^c 21.8 (AG → GA) ^c	5 5 5

a. $\Delta G^\ddagger$ and $\Delta H^\ddagger$ are in kJ mol^{-1} ; $\Delta S^\ddagger$ in $\text{J mol}^{-1} \text{K}^{-1}$.

b. Rot = rotation about the C-N bond; Inv = nitrogen inversion-rotation.

c. See figure 9.

References: 1. Bushweller *et al* (1974b); 2. Bushweller *et al* (1975); 3. Bushweller *et al* (1977); 4. Berger and Hobbs (1978); 5. Bushweller *et al* (1982).

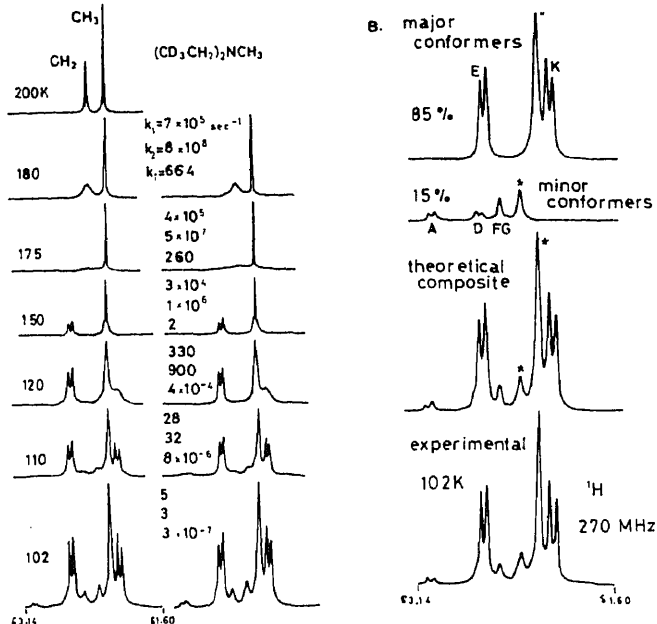


Figure 8. A: Experimental ^1H DNMR spectra (270 MHz) of $(\text{CD}_3\text{CH}_2)_2\text{NCH}_3$ (61; 2% v/v in CBrF_3) in the left column and theoretical DNMR simulations in the right column. k_1 is the first-order rate constant for inversion at nitrogen. k_2 is the rotation rate constant for conversion from a family of minor conformers (AG or GA; figure 9) to a family of major conformers (GG). B: Theoretical decomposition of the ^1H DNMR spectrum of $(\text{CD}_3\text{CH}_2)_2\text{NCH}_3$ at 102 K. The asterisks indicate the positions of the NCH_3 singlets. Reprinted with permission from Bushweller *et al* (1982).

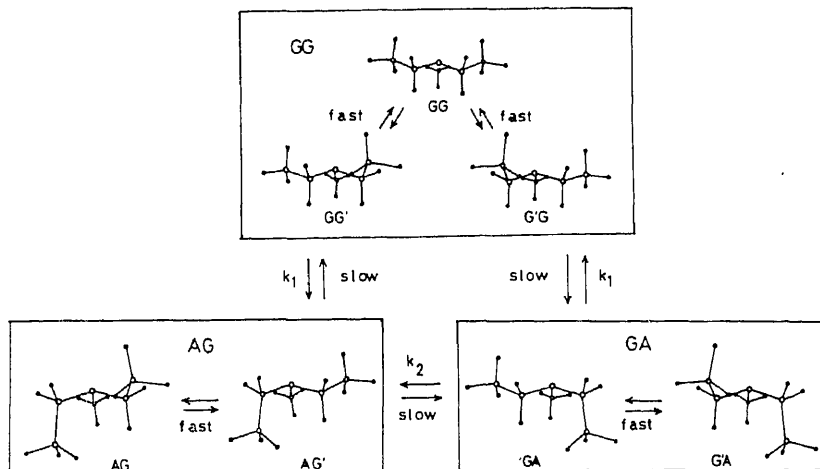
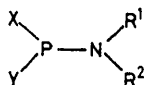


Figure 9. Proposed families of rotamers of $(\text{CD}_3\text{CH}_2)_2\text{NCH}_3$. Each box contains a family

positional exchange of atoms bonded to phosphorus and pyramidal inversion at phosphorus and nitrogen atoms.

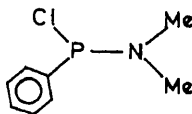
3.3a. *P(III)-N bond*: The dynamic stereochemistry of aminophosphines $\text{XYP-NR}^1\text{R}^2$ has been extensively studied by DNMR in recent years. The principal



points of interest in these studies have centred on evaluation of various factors which might influence the magnitude of the rotational barrier. In aminophosphines, the phosphorus and nitrogen atoms each possess lone pair electrons. Thus, another possible stereodynamical process is comprised of pyramidal inversions at either phosphorus or nitrogen atoms. However, phosphorus inversion is a relatively high energy process; the free energy of activation is $108.8 \text{ kJ mol}^{-1}$ for phosphorus pyramidal inversion in diphosphine (Lambert and Mueller 1966; Lambert *et al* 1968) and $\sim 125 \text{ kJ mol}^{-1}$ in tertiary phosphines (Horner and Winkler 1964), which are outside the range of energy normally approached by the NMR method. Thus, the phosphorus pyramidal inversion process can be excluded as a contributor to conformational change and the P-N bond rotation may be coupled only with the nitrogen inversion.

Since the measurement of the rotational barrier around the P-N bond in chloro(dimethylamino) phenylphosphine **1** was reported by Cowley *et al* (1968) using NMR bandshape analysis, the NMR observation in aminophosphines and related compounds has become popular and provided new evidences concerning the conformational preference at low temperatures and the relative importance of such factors as steric effects, lone pair-lone pair repulsion, and (*p-d*) π bonding in maintaining the preferred geometry.

The ^1H NMR spectrum for the methyl groups in chloro(dimethylamino) phenylphosphine **1** shows a doublet at ambient temperatures due to coupling of rotation-averaged methyl groups to the phosphorus atom. On cooling, the methyl doublet broadens and



1

eventually coalesces. Below 213 K, two clearly-defined doublets develop. At the coalescence temperature (223 K), $\Delta G^\ddagger = 45.6 \text{ kJ mol}^{-1}$ was obtained for the rotational barrier of the P-N bond (Cowley *et al* 1970b).

Among many workers, Cowley *et al* continued consistently their studies on stereochemical features of substituted aminophosphines by measuring the P-N bond rotational barrier using the DNMR bandshape method. The data obtained by Cowley *et al* (1970a, b) together with those of other workers are shown in table 17.

The data in table 17 show that increasing the steric bulk of the nitrogen substituents

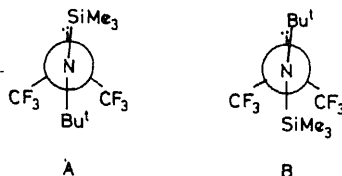
Table 17. Barriers to rotation about P(III)-N bond in aminophosphines.

No.	Compound	Solvent	T_c (K)	$\Delta G_f^\ddagger$ (kJ mol ⁻¹)	Reference
1.	PhP(Cl)-NMe ₂	CFCl ₃	223	45.6	1
	PhP(Cl)-NEt ₂	CFCI ₃ -CDCl ₃	216	45.2	1
	PhP(Cl)-NPr _{1/2}	CFCl ₃	258	53.6	1
	PhP(Cl)-NBu _{1/2}	CS ₂	288	61.1	1
2.	MeP(Cl)-NMe ₂	CH ₂ =CHCl	233	49.4	2
		Toluene-d ₈	233	47.3	2
	MeP(Cl)-NPr _{1/2}	CH ₂ =CHCl	253	56.1	2
		Toluene-d ₈	265	57.3	3
	MeP(Cl)-NBu _{1/2}	CDCl ₃	268	56.5	2
3.	Bu ^t P(Cl)-NMe ₂	CHFCI ₂	189	39.7	3
		CH ₂ =CHCl	188	39.3	2
	Bu ^t P(Cl)-NPr _{1/2}	CHFCI ₂	273	59.0	3
		CH ₂ Cl ₂	222	46.4	4
	Bu ^t P(Cl)-N(SiMe ₃) ₂	CH ₂ Cl ₂	200	44.4	4
4.	PhP(F)-NMe ₂	<i>n</i> -C ₆ H ₁₄	202	41.4	5
	MeP(F)-NPr _{1/2}	CH ₂ =CHCl	213	45.6	2
	MeP(F)-NBu _{1/2}	CHF ₂ Cl	223	45.2	2
5.	(CF ₃) ₂ P-NMe ₂	CF ₂ Cl ₂	168	36.4	1
			172	37.2	6
	(CF ₃) ₂ P-NHMe			~ 35.6	6
	(CF ₃) ₂ P-NEt ₂			41.8	7
	(CF ₃) ₂ P-NPr _{1/2}			61.9	7
	(CF ₃) ₂ P-NH(SiH ₃)	CHFCI ₂		< 30	7
	(CF ₃) ₂ P-N(Me)(SiH ₃)	CHFCI ₂		< 30	7
	(CF ₃) ₂ P-N(SiMe ₃) ₂	C ₆ H ₁₂		64.0	7
	(CF ₃) ₂ P-N(Bu ^t)(SiMe ₃)	CHFCI ₂		87.0	7
6.	(Me ₃ Si) ₂ CHP(Cl)-NMe ₂	CH ₂ Cl ₂	222	47.3	4
	(Me ₃ Si) ₂ CHP(Cl)-NPr _{1/2}	CH ₂ Cl ₂	248	53.1	4
7.	Cl ₂ P-NMe ₂	CHFCI ₂	160	35.1	1
	Cl ₂ P-NBu _{1/2}			71.1	8
	Cl ₂ P-N(Bu ^t)(SiMe ₃)	CHFCI ₂		53.6	7
	Cl ₂ P-N(SiMe ₃) ₂	C ₆ H ₁₂		41.8	7

References: 1. Cowley *et al* (1970b); 2. Distefano *et al* (1974); 3. Burdon *et al* (1976); 4. Goldwhite and Power (1978); 5. Simonnin *et al* (1972); 6. Cowley *et al* (1970a); 7. Neilson *et al* (1977); 8. Scherer and Kuhn (1975).

has an effect of increasing activation energies. Such trend is consistent with the argument that P-N bond rotation is, rather than nitrogen inversion, the rate-determining step in the above series of interconversions because increased steric congestion should increase the energy of the transition state of rotation.

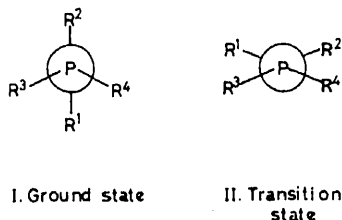
For example, (CF₃)₂P-N(SiMe₃)₂ and (CF₃)₂P-NBu^t(SiMe₃) (see series 5, table 17) exhibit unusually high P-N bond barriers of 64.0 and 87.0 kJ mol⁻¹, respectively. The ¹H and ¹⁹F NMR data for the latter indicate the presence of two rotational isomers. At



septets in the ^{31}P NMR spectrum of this compound at ambient temperatures. The high P–N bond barrier for these compounds can be attributed to the steric bulk of the nitrogen substituents.

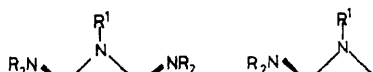
On the other hand, changing substituent R on phosphorus from Me to bulkier groups, Ph and Bu', in N,N-dimethylphosphonamidous chloride, $\text{R} \cdot \text{P}(\text{Cl})\text{NMe}_2$, decreases the barrier from 49.4 kJ mol^{-1} to 45.6 and to 39.7 kJ mol^{-1} , respectively. Also in N,N-diisopropylphosphonamidous chloride, $\text{R} \cdot \text{P}(\text{Cl})\text{NPr}_2$, changing from $\text{R} = \text{Me}$ to Ph decreases the P–N bond barrier from 56.1 to 53.6 kJ mol^{-1} (see table 17, compounds 1–3).

This barrier-decreasing steric effect of phosphorus substituents is generally observed in aminophosphines and arguments have been presented to explain this barrier lowering effect (Neilson *et al* 1977; Cowley *et al* 1976). From application of a perturbational molecular orbital model to H_2NPH_2 , it is predicted that the geometry at nitrogen should change from trigonal planar in the ground state (I) to pyramidal (II) when the dihedral angle between the lone pairs is increased from 90° to 180° in aminophosphines $\text{R}^3\text{R}^4\text{P}\text{--}\text{NR}^1\text{R}^2$ (Whangbo and Wolfe 1976; Cowley *et al* 1976). Accordingly, the P–N torsional barrier is not a pure rotational barrier as described

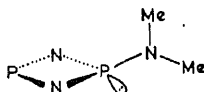


before; it is comprised of both P–N rotation and pyramidal inversion at nitrogen. Increasing the steric bulk of the nitrogen substituents R^1 and R^2 renders it more difficult for them to adopt the requisite nonplanar geometry at this centre in a transition state, increasing the rotational barrier. On the contrary, increasing the size of the phosphorus substituents R^3 and R^4 promotes pyramidity at nitrogen in a transition state, and the resulting steric acceleration causes a lowering of the observed barrier.

Bullock *et al* (1977a, b) prepared various derivatives of dialkylaminocyclodiphosphazane **8** and found that in some of them a mixture of geometrical isomers was



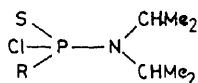
δ (NR)₃ (0.78–1.54 ppm). They suggested that the geometrical isomerism is due to the different mutual orientations of the exocyclic phosphorus substituent and that the isomer with the low-field ^{31}P signal should be tentatively assigned to the *cis* form and that with the high-field ^{31}P shift to the *trans* form. From the fact that the N-methyl protons of these derivatives ($\text{R}^1 = \text{R}^2 = \text{Me}$) are anisochronous in ^1H NMR spectra, it is inferred that the preferred conformation is one in which the methyl groups lie in, or close to, the plane passing through the two phosphorus atoms and perpendicular to the cyclodiphosphazane ring in which the ring nitrogen atoms have a planar or near planar configuration. The lone pair of electrons on nitrogen lies orthogonal to the lone pair on phosphorus.



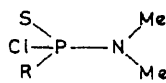
The rotational barriers to the exocyclic P–N bond in dialkylaminocyclodiphosphazanes which were obtained by ^1H NMR spectra for the exocyclic alkylamino groups are shown in table 18. In the table, for example, of the two values of barriers for compound **9** the first is that with a low-field ^{31}P shift, *i.e.* the *cis* form, which has a higher barrier than the second, *i.e.* the *trans* form. In general, there is a large difference of 12–26 kJ mol^{–1} in the barrier between *cis* and *trans* forms. The reason for this difference is not yet clear.

Changing the dimethyl group to diisopropyl on exocyclic nitrogen increases the barrier from 70.7 to 81.6 kJ mol^{–1} for compounds **17** and **19**. A similar trend is apparent upon changing the dimethyl group in compound **11** ($\Delta G^\ddagger = 52.7$ kJ mol^{–1}) to a diethyl group in compound **15** ($\Delta G^\ddagger = 57.7$ kJ mol^{–1}). These effects indicate steric dependence on the size of exocyclic dialkylamino groups. Increasing the size of the substituents on the ring nitrogen also increases the barrier. For example, compound **10** has a higher barrier than does **9**. This indicates a steric dependence on the ring nitrogen substituents.

3.3b. *P(V)–N bond*: Burdon *et al* (1976) reported the NMR investigation on phosphonamidothioic chlorides **24** and **25**. The ^1H NMR spectra for N,N-



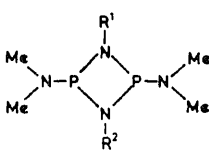
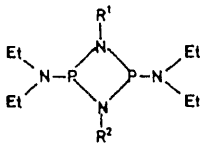
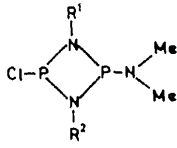
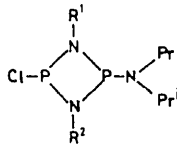
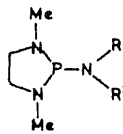
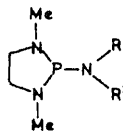
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diisopropylphosphonamidothioic chlorides **24** at ambient temperatures display two isopropyl methyl doublets. On cooling the two methyl doublets collapse and eventually separate into four doublets of equal intensity. Clearly the isopropyl groups become nonequivalent due to slow rotation around the P–N bond. Burdon *et al* (1976) obtained the free energy of activation for the P–N bond rotation derived by the bandshape analysis for the isopropyl methyl signals. Their data for these compounds are given in table 19. The data show that in phosphonamidothioic chlorides the P–N bond rotational barriers increase from methyl to isopropyl group on nitrogen and decrease

Table 18. Barriers to rotation about exocyclic P(III)-N bond.

No.	Compound	Substituents	Solvent	T_c (K)	$\Delta G_T^\ddagger$ (kJ mol ⁻¹)	Reference	
9.		R ¹ Bu ^t	R ² Me	CDCl ₃	239	52.3	1
10.		Bu ^t	Bu ^t	C ₆ H ₆	327	73.6	1
11.		Ph	Ph	CDCl ₃	252	52.7	1
12.		R ¹ = R ² = <i>p</i> -ClC ₆ H ₄		CDCl ₃	253	52.7	1
13.		R ¹ = R ² = <i>p</i> -MeC ₆ H ₄		CDCl ₃	250	52.3	1
14.		R ¹ = R ² = <i>p</i> -MeOC ₆ H ₄		CDCl ₃	254	53.1	1
15.		Ph	Ph	CDCl ₃	272	57.7	1
16.		Bu ^t	Me	CH ₂ Cl ₂	280	60.7	1
17.		Bu ^t	Bu ^t	Toluene	319	70.7	1
18.		Ph	Ph	CDCl ₃	260	56.1	1
19.		Bu ^t	Bu ^t	CDCl ₃	375	81.6	1
20.		Et	Et	CH ₂ Cl ₂	164	34.0	2
21.		Pr ⁱ	Pr ⁱ	CH ₂ Cl ₂	227	42.3	2

References: 1. Bulloch *et al* (1977b); 2. Hargis *et al* (1980).

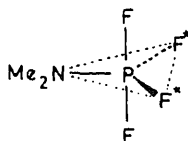
from methyl to phenyl on phosphorus increasing, however, for a *t*-butyl group on phosphorus.

Stereochemical processes in substituted derivatives of aminofluorophosphoranes 26–28 are very interesting, because in addition to P–N bond rotation, must be considered the possibilities of the concomitant occurring of other processes, *i.e.* fluorine atom permutation, pyramidal inversion at nitrogen, and rotation around the C–N bond in compounds of the type R₁R₂NPF₄, 26. Muetterties *et al* (1972) calculated the

Tabl 19. Barriers to rotation about P(V)-N bonds.

No.	Compound	Substituent	Solvent	T_c (K)	$\Delta G_T^\ddagger$ (kJ mol ⁻¹)	Reference
24.		R Me Ph Bu ^t	CH ₂ Cl ₂ CH ₂ Cl ₂ CH ₂ Cl ₂	207 208 244	43.1 42.3 52.7	1 1 1
25.		Ph Bu ^t	CH ₂ Cl ₂ CH ₂ CHCl	< 173 < 133	< 34 < 29	1 1
26.	PF ₄ -NMe ₂				39.7	2
27.	PF ₃ -(NH ₂) ₂		CH ₃ CN-CH ₂ Cl ₂	250	51.25 ($\Delta H^\ddagger = 44.56$ kJ mol ⁻¹) ($\Delta S^\ddagger = -26.8$ J mol ⁻¹ K ⁻¹)	2
28.	PF ₄ -NPr ₂ ⁱ			210 (C-N)	42	3
29.		X = Y = O (trans) (cis) X = Y = S (trans) (cis) X = Y = Se (trans) (cis) { X = S Y = lone pair	CDCl ₃ CH ₂ Cl ₂ CDCl ₃ CH ₂ Cl ₂ CDCl ₃ CH ₂ Cl ₂ CH ₂ Cl ₂	294 213 256 219 248 224 < 183	66.5 48.5 57.7 49.4 56.5 50.2 < 37 (for P(V)-N) 62.3 (for P(III)-N) 295 61.1 (for P(V)-N) 352 77.8 (for P(III)-N)	4 4 4 4 4 4 4 4 4 4

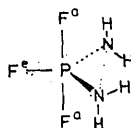
References: 1 Burdon *et al* (1976); 2 Muetterties *et al* (1972); 3 Cowley *et al* (1975); 4 Keat *et al* (1977).



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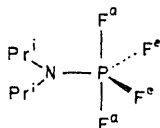
suggesting that the P–N bond rotation and Berry rearrangement are inextricably coupled.

The temperature dependent ^{19}F NMR spectra simulated on the basis of the completely uncorrelated internal rotation about the two P–N bonds in compound **27** are in excellent agreement with the observed spectra (Muetterties *et al* 1972). This indicates that the rotation about the two equivalent P–N bonds in $\text{PF}_3(\text{NH}_2)_2$ must be essentially uncorrelated.



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Diisopropylaminotetrafluorophosphorane **28** is also an interesting molecule for DNMR study, because information about several stereochemical processes is obtained by ^1H , ^{19}F , ^{31}P and ^{13}C NMR spectra (Cowley *et al* 1975). The ambient temperature ^1H and



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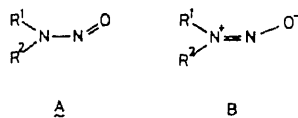
^{13}C spectra indicate that the isopropyl methyl and methine proton (or carbon) atoms are equivalent at those temperatures. The ^{19}F spectrum consists of a doublet, thereby indicating that the axial and equatorial fluorine environments are being averaged. The 253 K ^{31}P spectrum is a quintet of triplets. Thus, it seems that above 253 K, the fluorine permutation, the P–N bond rotation, the pyramidal inversion at nitrogen and the N–C bond rotation are rapid on the NMR time scale. The ^{19}F spectrum at 163 K indicates that the equatorial fluorines are equivalent but the axial fluorines are nonequivalent due to the different orientations of the isopropyl groups at this temperature. On cooling from 253 K to 173 K the ^{31}P spectrum changes from a quintet of triplets to a quintet of

hence the barrier for fluorine permutation represents a lower limit to the barrier to the P-N bond rotation.

The measurements of rotational barriers to the exocyclic P-N bond in 2,4-bis(dimethylamino)-1,3-ter-butylcyclo-diphosph(V)azane derivatives **29** have been reported by Keat *et al* (1977). The observation of nonequivalent N-methyl groups in ^1H NMR spectra at low temperature indicates the ground state conformation in which methyl groups lie in, or near, the plane passing through the phosphorus atoms and perpendicular to the ring plane as in diphosph(III)azanes. This conclusion is confirmed by the x-ray analysis of the *cis* isomer. The *cis* and *trans* isomers of these compounds were separated and the free energies of activation, $\Delta G^\ddagger$ were determined. The values are included in table 19.

3.4 Nitrogen-nitrogen bond

3.4a. *Nitroso compounds*: It has been known for more than twenty years that N-nitrosamines exhibit isomerism due to restricted rotation about the N-N bond (Looney *et al* 1957). Contributions from the mesomeric forms **A** and **B** of the N-



nitrosamine group produce a planar structure in which the NNO group and α -carbon atoms are coplanar. The barrier to rotation about the N-N bond of nitrosamines stems largely from the partial double bond character of the N-N bond. The fact that trifluorodimethylnitrosamine, $(\text{CF}_3)_2\text{NNO}$ (**2**, table 20), has a barrier of only $\sim 20 \text{ kJ mol}^{-1}$ confirms this basic hypothesis, because the presence of two electron-withdrawing groups CF_3 at R^1 and R^2 reduces the prevalence of the mesomeric form **B**. Table 20 summarizes the rotational barriers about N-N bonds found in nitroso compounds.

The room temperature proton magnetic resonance spectrum of dimethylnitrosamine **1**, Me_2NNO , consists of two sharp signals of equal intensity. The internal chemical shift between the two methyl groups *cis* and *trans* to the nitroso group would be ascribed to electric field effects between the oxygen atom and the methyl groups situated at different distances from the oxygen atom. In such a field effect the downfield resonance would ordinarily be assigned to the methyl group *cis* to the oxygen atom and the upfield resonance to the methyl group *trans* to the oxygen atom. However, this assignment of methyl proton resonances was reversed by later work (Brown and Hollis 1964; Karabatsos and Taller 1964) in which isomer ratios in unsymmetrical nitrosamines and a considerable variation in the chemical shift differences between protons *cis* and *trans* to the nitroso group in dialkyl nitrosamines was investigated.

The first report concerning the restricted rotation about the N-N bond in aromatic N-nitrosamines was made by Forlani *et al* (1979). A bandshape analysis of the ^{13}C spectra for N-nitrosodiphenylamine **6** and N-nitrosocarbazole **7** give activation free energies, $\Delta G^\ddagger$ of 79.9 and of 70.5 kJ mol^{-1} , respectively. The fact that the barrier of N-nitrosocarbazole **7** is lower than that in N-nitrosodiphenylamine **6** is due to the rigidity of the carbazole ring making the whole molecule perfectly planar, thus the con-

Table 20. Barriers to rotation about N-N bond in nitroso compounds^a.

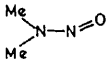
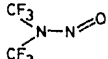
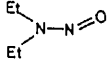
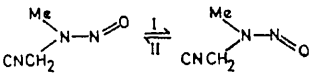
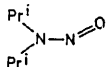
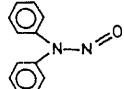
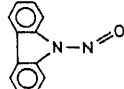
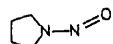
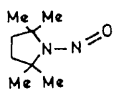
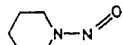
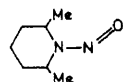
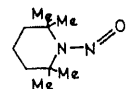
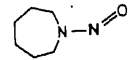
No.	Compound	Solvent	$\Delta G^\ddagger$ (T)	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
1.		Neat	97.0 (450)			1
		Nitrobenzene	96.2			2
2.		Neat	~ 20			3
3.		Nitrobenzene	97.1	96.7	1.2	2
4.		(CCl ₃) ₂ CO		(I) 79.1 (II) 80.0	-15.5 -14.2	4
5.		Nitrobenzene	98.3	98.3	0.6	2
6.	 Nitrosopyrrolidine	DMSO-d ₆	79.9			5
7.		DMSO-d ₆	70.5	73.2	8	5
8.	 Nitrosopiperidine	Neat	99.6 (298)		-13.8	6
9.		Benzonitrile	> 95 (> 433)			7
10.		Neat	100.4 (298)	97.9	-7.5	6
		Neat	93.0 (450)			1
11.		Nitrobenzene	82.0			2
		TCE	79 (376)			7
12.		TCE	82.2			8
		Benzonitrile	87 (401)			7
13.		Neat	> 97.5 (> 200)			6
14.		Neat	> 98.3 (> 200)			6

Table 20. (Continued)

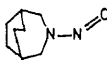
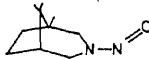
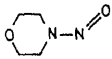
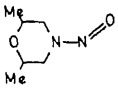
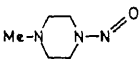
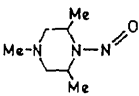
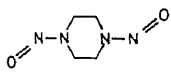
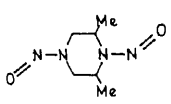
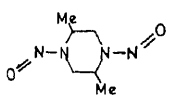
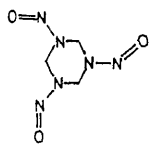
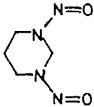
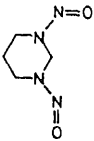
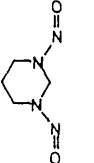
No.	Compound	Solvent	$\Delta G^\ddagger$ (T)	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
15.		<i>o</i> -DCB	108.4 (298)	118.8	34.7	6
		DPE	105.0 (298)	108.4	11.7	6
		<i>o</i> -DCB	~ 100 (> 448)			6
		DPE	102.5 (298)	102.5	0.8	6
	Nitrosomorpholine					
16.		Benzonitrile	85 (449)			7
17.		Benzonitrile	91 (407)			7
	Nitrosopiperazine					
18.		Benzonitrile	92 (438)			7
19.		Benzonitrile	80 (376)			7
20.		DMF-d ₇	93.39 (400)			9
21.		PCB/BZ	76.40 (400)			9
22.		DMF-d ₇	(I) ^c 98.99 (400) (II) 90.67 (400)			9
23.		DMF-d ₇	(I) ^c 76.11 (340) (II) 75.48 (340) (III) 76.90 (340)			9
24.		Benzonitrile	77 (371)			7

Table 20. (Continued)

No.	Compound	Solvent	$\Delta G^\ddagger$ (T)	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
25.		<i>p</i> -DCB	83.5 (450)			1
		<i>p</i> -DCB	83.0 (450)			1
		<i>p</i> -DCB	85.0 (450)			1

a. $\Delta G^\ddagger$ and $\Delta H^\ddagger$ are in kJ mol^{-1} ; $\Delta S^\ddagger$ in $\text{J mol}^{-1} \text{K}^{-1}$; T in Kelvin.

b. DCB = *o*-dichlorobenzene; TCE = tetrachloroethane; DPE = diphenylether; PCB = perchlorobutadiene; BZ = benzene.

c. See the text about I, II and III.

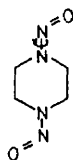
References: 1. Glidewell (1977); 2. Lunazzi *et al* (1976c); 3. Andreadas (1962); 4. Szymanski *et al* (1977); 5. Forlani *et al* (1979); 6. Cooney *et al* (1974); 7. Harris *et al* (1980); 8. Lunazzi and Macciantelli (1981); 9. Höfner *et al* (1978c).

tribution of the above N-phenyl conjugate form is increased (Forlani *et al* 1979). The barriers of the aromatic N-nitrosamines are lower than those of aliphatics. The dipole form **B** in mesomery is more favoured in aliphatics than in aromatics. Since the sp^3 nitrogen can conjugate with the aromatic ring, the N–N double bond character is reduced.

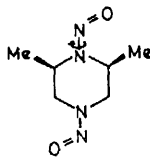
A ring size effect on the energy barrier to rotation was not clearly observed; the barriers, as shown in table 20, do not increase linearly as the ring size increases from N-nitrosopyrrolidine **8** (5-membered) to N-nitrosopiperidine **10** (6-membered) to **13** (7-membered) and to **14** (8-membered) (Cooney *et al* 1974). The value for *cis*-2,6-dimethyl-4-nitrosomorpholine **17** is substantially higher than that for unsubstituted morpholine **16**, which can perhaps be accounted for by the additional rigidity of the ring for the substituted morpholine, the methyl groups being constrained to be equatorial (Harris *et al* 1980).

Höfner *et al* (1978c) detected two isomers each in 1,4-dinitrosopiperazine **20**, *cis*-2,6-dimethyl-1,4-dinitrosopiperazine **21**, and 1,3,5-trinitrosohexahydro-*s*-triazine **23**, and three isomers each in *trans*-2,5-dimethyl-1,4-dinitrosopiperazine **22** by using the ring hydrogen atoms as sensor nuclei for **20** and **23**, and the methyl signals for **21** and **22** in

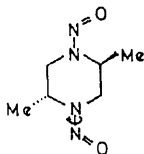
to rotation about one N-N bond was detected in compound **21**. The free energies of activation, $\Delta G^\ddagger$ (kJ mol^{-1}), corresponding to various rotational processes in each compound have been obtained by total ^1H NMR bandshape analysis (Höfner *et al* 1978c) and included in table 20.



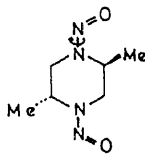
20



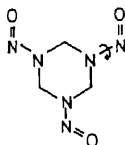
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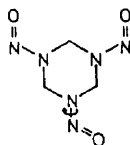
22(I)



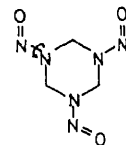
22(II)



23(I)

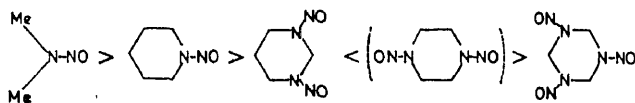


23(II)



23(III)

As there is not a significant difference between the values of $\Delta G^\ddagger$ for dimethylnitrosamine **1** and N-nitrosopiperidine **10**, it seems likely that ring strain is not the cause of any differences. The differences in the barrier to rotation about the N-N bond in six-membered ring compounds, therefore, are likely of electronic nature. For dinitrosopiperazine **20**, dinitrosopyrimidine **25**, and trinitrosotriazine **23**, if all the nitroso groups in a ring were of mesomeric form (**B**), then there would be increasing amount of positive charges in proximity across the ring as the number of nitroso groups increase. From the above consideration, Glidewell (1977) predicted that observed barriers for mono-, di- and tri-nitroso compounds would decrease sequentially. However, as shown in the following series, 1,4-dinitrosopiperazine **20** is out of place.



1

10

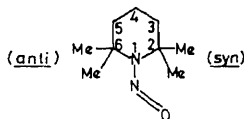
25

20

23

The barrier for 1,4-dinitropiperazine **20** is very close to the values for 1-methyl-4-nitrosopiperazine **18** and for mononitrosopiperidine **10**. Thus, the two nitroso groups in dinitrosopiperazine appear to behave independently, an argument which is consistent with the conclusion that concerted double rotations are completely absent in **20** and related compounds (Höfner *et al* 1978c; Harris *et al* 1980).

In the N-nitroso-2,2,6,6-tetramethylpiperidine **12** the N=O moiety is coplanar with the virtual plane of the ring, *i.e.* it is perpendicular to the symmetry plane bisecting the



12

piperidyl ring through nitrogen and carbon-4 (Lunazzi *et al* 1976c, 1977b, 1978, 1980a; Lunazzi and Macciantelli 1981). As shown in figure 10, at -115°C , two carbons of methyls *syn* and *anti* to the NO group give upfield and downfield signals, respectively, and each of C-2,6 and C-3,5 display two signals. This is consistent with slow N-N rotation and with the planar conformation. Below -130°C , the signal for the *syn*-methyl carbons broadens indicating slowing of ring reversal and at -152°C , splits into two signals corresponding to one axial (upfield) and one equatorial (downfield) methyl which is superimposed on the signal for the pair of methyls *anti* to the NO group. Similar results have been obtained for N-nitroso-2,6-dimethylpiperidine **11**. From these evidences it has been concluded that methyl substituted nitrosopiperidine has the coplanar conformation.

Adopting the coplanar conformation for dimethylnitrosopiperidine **11**, in order to avoid the $A^{(1,3)}$ type strain, *viz.* non-bonding interaction between the N-substituent (*i.e.*

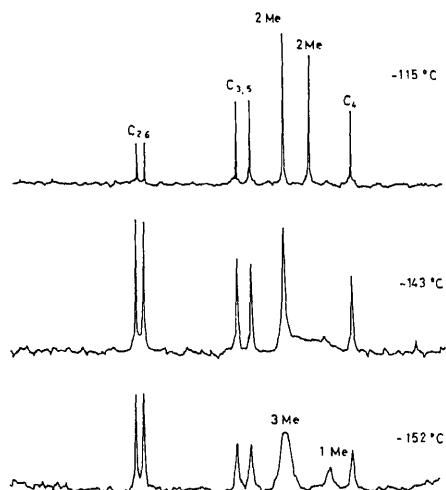
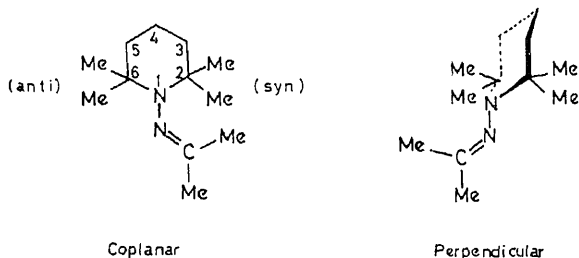


Figure 10. Temperature dependence of the ^{13}C spectrum of N-nitroso-2,2,6,6-tetra-

the ground state and raise its energy level by the energy corresponding to this interaction (Chow *et al* 1968; Harris *et al* 1980). On the other hand, in the transition state, the $A^{(1,3)}$ interaction is released and the ring is no longer constrained to the form with the methyls axial. So, the barriers to N-N bond rotation are lower in dimethyl substituted piperidine **11** and piperazine **21** than those for the unsubstituted compounds **10** and **20**, respectively. Chow *et al* (1968) have estimated the diaxial methyl-methyl interaction energy in N-nitroso-2,6-dimethylpiperidine **11** to be about 16 kJ mol^{-1} as a difference between the N-N rotational barrier in **11** and in dimethylnitrosamine **1** in which a diaxial methyl-methyl interaction is not expected. In fact, the barrier $\Delta G^\ddagger$ to the N-N bond rotation in N,N-dinitroso-2,6-dimethylpiperazine **21** ($\Delta G^\ddagger$: 76.4 kJ mol^{-1}) is 17.0 kJ mol^{-1} lower than the $\Delta G^\ddagger$ of $93.39 \text{ kJ mol}^{-1}$ for unsubstituted dinitrosopiperazine **20**. The difference of barriers between these two compounds corresponds to the axial methyl-methyl interaction energy.

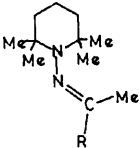
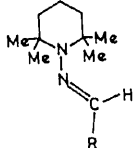
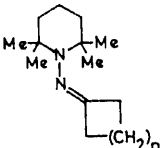
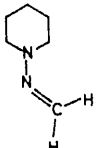
3.4b. *Hydrazones*: Lunazzi *et al* (1976c, 1977b, 1981) synthesized a number of hydrazone derivatives and investigated intensively the restricted rotation about the N-N bond and other stereodynamical motions in hydrazones by using ^1H and ^{13}C NMR spectroscopy. In contrast to the evidences for the restricted N-N bond rotation in N-nitrosoamines, $\text{R}_2\text{N}=\text{N}=\text{O}$, mentioned in the previous section, nonequivalence of the R protons in the corresponding hydrazones $\text{R}_2\text{N}=\text{N}=\text{CR}'_2$ is not observed. Lunazzi *et al* (1976c) suggested that the barriers to the N-N bond rotation in the aliphatic hydrazones are probably lower than 25 kJ mol^{-1} . On the other hand, the hydrazones containing a piperidyl ring (26–43), pyrazolidindione (**44**) and pyrimidintrion (**45**) rings show evidence of restricted rotation about the N-N bond in both ^1H and ^{13}C NMR spectra (table 21).

The majority of compounds considered for discussion here are the piperidyl hydrazones **26–43** studied by Lunazzi *et al* (1976c). There is some experimental



evidence for assuming a perpendicular conformation in the ground state of hydrazone derivatives, unlike the case of N-nitrosopiperidine. The determination as to whether the conformation for the ground state of hydrazones is coplanar or perpendicular has been made by the ^{13}C NMR spectrum. In contrast to the spectrum (figure 10) for the N-nitrosopiperidine derivatives whose ground state is coplanar, the ^{13}C NMR spectrum (figure 11) for 2,2,6,6-tetramethyl-1-[1-(3-pyridyl)-ethylideneamino] piperidine (**29** in table 21) shows that the pairs of methyl groups are nonequivalent and a

Table 21. Barriers to rotation about N-N bond in hydrazones^a.

No.	Compound	Substituent: R	Solvent	$\Delta G^\ddagger$ (T)	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
							
26.		Me	C ₂ Cl ₄	69.9 (328)	72.0	6.3	1
			C ₆ H ₅ NO ₂	69.0 (326)	71.1	5.9	1
			CHF ₂ Cl	65.3			2
27.		Ph	CDCl ₃	65.3 (309)			1
28.		4-pyridyl	CDCl ₃	59.0 (280)	59.0	0.4	3
29.		3-pyridyl	CDCl ₃	62.3 (295)	65.3	10.5	3
30.		2-pyridyl	CDCl ₃	58.2 (274)			3
31.		trienyl	CDCl ₃	60.2 (285)			3
32.		2-furyl	CDCl ₃	59.8 (282)			3
							
33.		H	CHF ₂ Cl	31.6 (151)			1
			CHF ₂ Cl	30.5			2
34.		Me	CHF ₂ Cl	37.2 (182)			1
35.		α -naphthyl	CHF ₂ Cl	35.6 (169)			4
36.		β -naphthyl	CDCl ₃	66.9 (316)			4
37.		$-\text{C}(\text{CH}_2\text{CMe}_2)_4$	C ₂ Cl ₄	69.0 (327)			4
38.		$-\text{CH}(\text{CMe}_2)_5$	C ₂ Cl ₄	71.1 (334)			4
							
39.		n = 1	CS ₂	48.5 (226)	48.1	-0.8	1
		n = 2	CDCl ₃	60.0 (279)	57.5	-8.8	1
		n = 3	C ₂ Cl ₄	75.3 (352)	74.9	-1.6	1
		n = 4	C ₂ Cl ₄	73.2 (340)	74.1	2.5	1
		n = 5	C ₂ Cl ₄	72.0 (335)	72.8	2.1	1
		n = 9	C ₂ Cl ₄	76.1 (356)			1
40.			CHF ₂ Cl	20.9 (113)			2
41.			Me ₂ O	36.8 (ring reversal)			2

42.		29-7 (ring reversal) 29-3 (N-N rotation)
43.		29-9 (ring reversal) 29-3 (N-N rotation)
44.		Ph ₂ O 73.7 (346) (N-N rotation) C ₆ H ₅ NO ₂ 74.2 (350) (N-N rotation)
45.		R = Ph R = Me Ph ₂ O 70.0 (320) (N-N rotation) C ₆ H ₅ NO ₂ 67.0 (314) (N-N rotation) 80.0 (361) (C=N rotation)

a. $\Delta G^\ddagger$ and $\Delta H^\ddagger$ are in kJ mol^{-1} ; $\Delta S^\ddagger$ in $\text{J mol}^{-1} \text{K}^{-1}$; T in Kelvin.

References: 1. Lunazzi *et al* (1976c); 2. Lunazzi and Macciantelli (1981); 3. Lunazzi *et al* (1977b); 4. Lunazzi *et al* (1977b); 5. Kölle *et al* (1980).

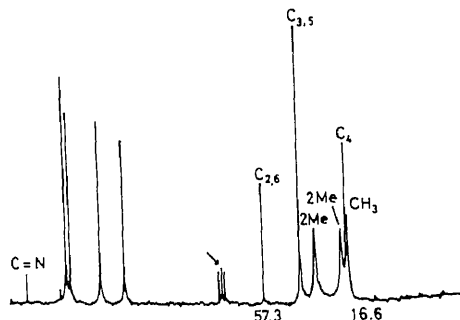


Figure 11. ^{13}C NMR spectrum of 2,2,6,6-tetramethyl-1-[1-(3-pyridyl)ethyldene]piperidine (29; in CDCl_3) at room temperature. Reproduced from Lunazzi *et al* (1977b) with permission of Royal Society of Chemistry.

single line for both C-2,6 and C-3,5 does not split, indicating the pairs of carbons are equivalent to each other. Obviously this spectral pattern can only be displayed when the plane of $-\text{N}=\text{C}$ is perpendicular to the piperidyl ring (Lunazzi *et al* 1977b).

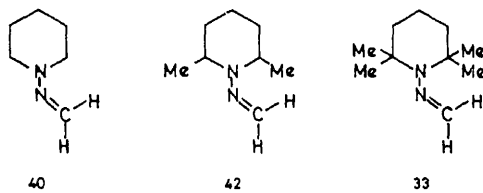
Perusing the data listed in table 21, the barrier to N-N bond rotation increases with increasing size of the iminyl group. This indicates that the perpendicular conformer

is preferred for the ground state of tetramethylpiperidyl hydrazones, because the transition state (coplanar) occurring by 90° rotation of the N–N bond is destabilized by steric interaction between the piperidyl methyl group and the iminyl group. Thus, the barrier should increase as the iminyl group gets larger. In case the ground state adopts the coplanar conformation, a quite reversed phenomena will occur which is not in accord with the experimental results.

That the N–N rotational barrier (30.5 kJ mol^{-1}) for compound **33** is substantially lower than that for compound **26** (65.3 kJ mol^{-1}) is due to the smaller steric hindrance experienced by the $\text{N}=\text{CH}_2$ group in **33** with respect to the bulkier $\text{N}=\text{CMe}_2$ group in **26** (Lunazzi and Macciantelli 1981). Although steric hindrance plays the most important role in determining the rotational barrier for hydrazones, electric properties have also some effects. On comparing those barriers for compounds **27**, **37** and **38**, it seems clear that the larger the conjugative ability, the smaller the rotational barrier. This trend is also exhibited by the three pyridyl hydrazones **28**, **29** and **30**. Among these compounds, *meta*-pyridylhydrazone **29** is expected to have a smaller conjugative ability with respect to the *ortho*- and *para*-derivatives, **30** and **28**, thus **29** has a larger barrier (Lunazzi *et al* 1977b).

In N-aminotetramethylpiperidine **41**, ring reversal is the only motion that can generate two signals of equal intensity for the two pairs of methyl groups. Below -80°C , two ^{13}C signals were detected for the two pairs of axial and equatorial methyl groups, the barrier to ring reversal being found to be 36.8 kJ mol^{-1} (Lunazzi and Macciantelli 1981).

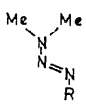
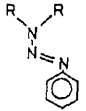
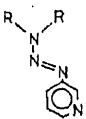
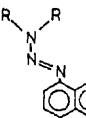
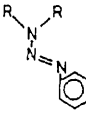
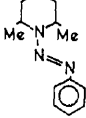
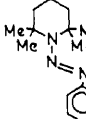
2,6-*cis*-dimethyl-1-methylideneaminopiperidine **42** seems to have an intermediate steric effect, between that of the hydrazone with an unsubstituted piperidine ring, **40** (coplanar conformation), and that of hydrazone with a piperidine ring substituted by two pairs of methyl groups, **33**. If the two methyls in the piperidiny ring of **42** are axial,



the steric effect experienced by the $\text{N}=\text{CH}_2$ group of a dimethyl piperidiny hydrazone should be similar to that of the unsubstituted hydrazone **40**. On the other hand, if the methyl groups are equatorial, the steric effect will be very close to that of tetramethyl piperidiny hydrazone **33**. From the ^{13}C NMR spectrum for hydrazone **42** at -138°C , Lunazzi and Macciantelli (1981) have suggested that there are two arrangements of different stability; namely one is an arrangement with methyl oriented axially and another with the methyl equatorial. In the equatorial methyl arrangement, the $\text{N}=\text{CH}_2$ group adopts a perpendicular conformation as in the compound **26**, and in the axial methyl arrangement, the $\text{N}=\text{CH}_2$ group is coplanar as in the compound **40**.

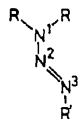
3.4c. Triazenes: As shown in table 22, rotational barriers about the N(1)–N(2) bond in 1,1-dialkyl-3-alkyl (**46**) and -3-aryl (**47–52**) triazenes have been measured by the line-

Table 22. Barriers to rotation about N-N bond in triazenes^a.

No.	Compound	Substituent: R	Solvent	$\Delta G^\ddagger$ (T)	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Ref.
46.		R = Bu ⁿ R = CH ₂ Ph	CD ₂ Cl ₂ CD ₂ Cl ₂	43.9 (228) 44.8 (231)			
47.		R = Me R = Et R = Pr ⁱ	CS ₂ CS ₂ CS ₂	57.7 (299) 57.7 60.2	59.8 65.3	7.1 18.8	
48.		R = Me R = Et R = Pr ⁱ	CS ₂ CS ₂ CS ₂	63.6 62.3 64.9			
49.		R = Me R = Pr ⁱ	CS ₂ CS ₂	60.2 61.5			
50.		R = Me R = Pr ⁱ	CS ₂ CS ₂	59.4 61.5			
51.			CS ₂	45.2			
52.			CS ₂	44.4			

a. $\Delta G^\ddagger$ and $\Delta H^\ddagger$ are in kJ mol⁻¹; $\Delta S^\ddagger$ in J mol⁻¹ K⁻¹; T in Kelvin.

References: 1. Sieh *et al* (1980); 2. Lunazzi *et al* (1978).



(R = alkyl or aryl)



the barrier is only slightly affected by the bulkiness of the aryl groups. The pyridyl derivatives have relatively higher barriers because the pyridyl ring stabilizes the mesomeric form **B** more than do phenyl or naphthyl groups. The dimensions of aromatic rings do not affect the barrier, since both the α - and β -naphthyl derivatives **49** and **50** have barriers very similar to those of the corresponding phenyl-triazenes **47**, a situation opposite to that observed in hydrazones with aromatic substituents (Lunazzi *et al* 1978).

The salient features of triazenes containing the 2,6-*cis*-dimethyl (**51**) or 2,2,6,6-tetramethylpiperidyl (**52**) ring are to have much lower $\Delta G^\ddagger$ values (see table 22). Also in contrast to analogous hydrazones whose conformations are perpendicular to the average plane of piperidyl ring as previously stated, it has been demonstrated by ^{13}C NMR spectra that the compounds **51** as well as **52** are in a coplanar conformation. As shown in figure 12, the ^{13}C NMR spectra for both compounds display four signals due to

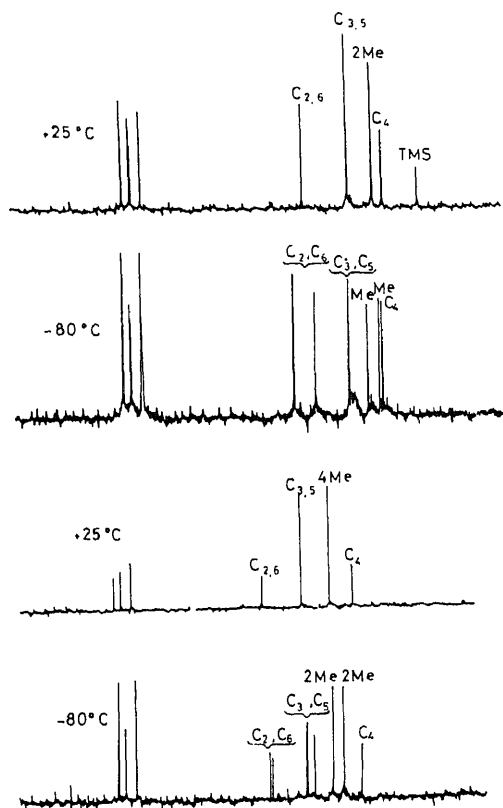
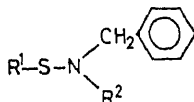


Figure 12. ^{13}C NMR spectra of phenyltriazenes containing 2,6-*cis*-dimethyl- and 2,2,6,6-tetramethylpiperidyl groups (**51**, upper two traces; and **52**, lower two traces, respectively).

C-2,6, C-3,5, C-4 and methyl carbon at room temperature. However, at -80°C the split into two pairs with the exception of C-4. Thus Lunazzi *et al* (1978) conclude both compounds are in a coplanar conformation, differing from the analogous hydrazones. The methyl groups on the piperidinyl ring of compound **51** adopt a chair conformation as in N-nitroso-dimethylpiperidine. The axial-axial repulsion of the methyl groups destabilizes the ground state of this compound, thus lowering the energy as aforementioned. However, in 2,2,6,6-tetramethylpiperidinyltriazene **52**, in addition to the repulsion between the two axial methyl groups, the $A^{(1,3)}$ strain between the axial substituent and the equatorial methyl groups inevitably exists. Lunazzi *et al* suggested that the tetramethylpiperidyl ring is in a twisted conformation, thus, because of the axial-axial repulsion and the $A^{(1,3)}$ strain can be released to some extent, and the ground state can become more stable than the chair conformation.

3.5 Sulfur–nitrogen bond

The ^1H NMR spectra of N-alkyl-N-benzylsulfenamides; at low temperature, ex-

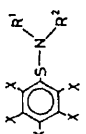
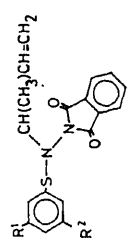
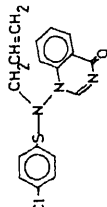
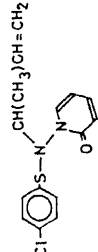
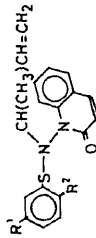


hibit a four-line AB system for the benzylmethylene hydrogens which are diastereotopic. As elevating temperatures, the AB quartets broaden, coalesce, and finally show a singlet, indicating that conformational interchanges occur rapidly on the NMR time scale. The coalescence of signals of diastereotopic methylene protons may be explained as associated with the sulfur or nitrogen inversion, or rotation about the S–N bond. However, inversion of the sulfur pyramid can be rejected as a contributor to the racemization because the barrier for inversion at sulfur is substantially greater than the barriers observed for the rotation about N–S bonds. Raban and his coworkers (Raban *et al* 1969; Raban and Jones 1971; Raban *et al* 1972; Raban and Yamamoto 1973) synthesized a number of sulfenamides and demonstrated that the rate-determining step for the conformational interchanges is associated with the rotation about the S–N bond rather than the nitrogen inversion. The barriers obtained by them are listed in table 1.

Raban and Jones (1971) observed interesting facts that when the sulfenyl phenyl group does not have polar substituents in alkyl-N-arenesulfonylarenesulfenamides, the substitution in the sulfonyl phenyl ring has no effect on the rotational barrier about the S–N bond, however, when the sulfenyl ring contains electron-withdrawing groups, electronegative substituents in the sulfonyl phenyl ring lower the barrier. In order to rationalize, in general, the existence of the substantial barriers to the S–N rotations in this series of compounds they proposed a partial S–N double bond mechanism in the rotational transition state which is caused by partial transfer of the nitrogen lone pair into a vacant *d*-orbital on sulfur, i.e. (*p*–*d*) π conjugation. However, this mechanism has been disputed by Kost *et al* (1980) to account for some experimental evidence.

Table 23. (Continued)

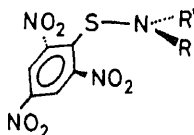
No.	Compound	Substituent	Solvent	Rotation observed	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	Refer
4.		X = <i>p</i> -CH ₃ ; X' = H X = X' = H X = <i>o</i> -NO ₂ ; X' = <i>p</i> -Me X = 2,4-(NO ₂) ₂ ; X' = <i>p</i> -Me X = 2,4,6-(NO ₂) ₃ ; X' = <i>p</i> -CH ₃	CDCl ₃ CDCl ₃ toluene-d ₈ toluene-d ₈ CDCl ₃		235 256 348 376 269	51.0 54.4 77.0 82.4 57.7	3 3 3 3 4
5.		R = CH ₂ C ₆ H ₅ R = CH(CH ₃) ₂ R = C(CH ₃) ₂ CH ₂ OCH ₃	C ₆ H ₅ CD ₃ C ₆ H ₅ CD ₃ C ₆ H ₅ CD ₃		341 388 416	71.1 84.1 89.5	5 1 5
6.		R = CH(CH ₃) ₂ R = 2,4,6-(CH ₃) ₃ C ₆ H ₂	toluene-d ₈ CDCl ₃		330 263	69.0 56.1	1 4 4
7.		R = CH ₂ C ₆ H ₅ R = CH(CH ₃) ₂ R = C(CH ₃) ₂ CH ₂ OCH ₃	CDCl ₃ CDCl ₃ CDCl ₃		294 262 314	61.1 59.4 65.3	5 5 5
8.		R = CH(CH ₃) ₂ R = 2,4,6-(CH ₃) ₃ C ₆ H ₂	toluene-d ₈ CDCl ₃		281 239	64.9 50.2	4 4 4
9.		X = 2,4-(NO ₂) ₂ X = 2,4,6-(NO ₂) ₃ X = H X = <i>p</i> -Cl	toluene-d ₈ toluene-d ₈ CH ₂ Cl ₂ CH ₂ Cl ₂		378 335 261 267	86.2 73.6 59.8 61.1	4 4 4 4

10.		$X = Cl; R^1 = R^2 = Pr^i$ $X = Cl;$ $R^1 = C(CH_3)_2CH_2OH;$ $R^2 = p-CH_3C_6H_4SO_2$ $X = F; R^1 = Pr^i;$ $R^2 = p-CH_3C_6H_4SO_2$ $X = F;$ $R^1 = C(CH_3)_2CH_2OCH_3;$ $R^2 = p-CH_3C_6H_4SO_2$ $X = F; R^1 = CHMePh;$ $R^2 = p-CH_3C_6H_4SO_2$	$CDCl_3$ $CDCl_3$	308 248	50.6 51.0
			CH_2Cl_2	238	50.6
			$CH_2Cl_2/CDCl_3$	258	54.4
			$CH_2Cl_2/CDCl_3$	226	47.7
			$CDCl_3$ $CDCl_3$	271 312	61.1 61.1
11.		$R^1 = NO_2; R^2 = H$ $R^1 = R^2 = NO_2$			
12.			toluene-d ₈	301	62.3 (N-N rotation)
13.			$CDCl_3$	305	63.6 (N-N rotation)
14.		$R^1 = Cl; R^2 = H$ $R^1 = H; R^2 = NO_2$	C_6H_5Cl C_6H_5Cl		109.2 (N-N rotation) 105.9 (N-N rotation)

References: 1. Raban and Jones (1971); 2. Kost *et al* (1980); 3. Raban *et al* (1972); 4. Raban and Yamamoto (1979); 5. Raban and Yamamoto (1977); 6. Atkinson *et al* (1979); 7. Atkinson *et al* (1978).

substitution by an electronegative group X would withdraw the nonbonding electron density from nitrogen, and should decrease the C–N rotational barrier. The experimental results (table 23) show that although S–N torsional barriers increase with increasing electron-withdrawing power of the substituents, the amide barriers show no substituent dependence. This has been interpreted by Kost *et al* to be evidence against the $(p-d)\pi$ mechanism for S–N rotation.

Introduction of a nitro group at the *ortho*-position of the sulfenyl phenyl ring results in a remarkable increase in the barrier to the S–N bond rotation as may be seen by comparison between compounds **4b**, **4c** and **4d**, thus leading to the expectation that compounds with two *ortho*-nitro groups will have substantial barriers. Contrary to that expectation, the barrier in 2,4,6-trinitrobenzenesulfenylsulfonamide **4e**, is significantly lower than that in **4d**. Another example is the barrier in N,N-diisopropyl-2,4,6-trinitrobenzenesulfenamide **9b** which is substantially lower than that in **9a**. Raban and Yamamoto (1977, 1979) suggested that when the second *o*-nitro group is introduced in the sulfenyl phenyl ring the CNS plane may be out of the plane of the phenyl ring because of substantial steric interaction between the two *o*-nitro groups and NR'R moieties. Such a change in the conformation of either the ground state or the transition state could account for the observed lowering of the barriers.



4. Intermolecular interactions and internal rotations

Like many other chemical phenomena, internal rotation of molecules has been observed to be affected by molecular interactions, of which solute-solvent interactions are most commonly encountered. In this section, the effect of molecular interactions on hindered internal rotation will be discussed in terms of nonspecific and specific interactions. The division is rather artificial and largely for convenience, because many types of interactions can coexist simultaneously in a system. Moreover, every interaction may be considered as specific if viewed microscopically and, for a rigorous treatment, deserves complete description of the position and orientation of all the interacting molecules around a solute molecule. If an interaction is relatively weak, however, the effect dependent on the positions and orientations of surrounding molecules may be considered as averaged and approximated in terms of bulk parameters, and the interaction may then be called non-specific. Many theories have been proposed for treatment of such interactions. A typical example is the reaction field theory which uses a model of a dipole in a cavity in a continuous dielectric medium. Permanent or induced dipole-dipole and dipole-quadrupole interactions may be included in such interactions, and will be the subject of §4.1. More specific molecular

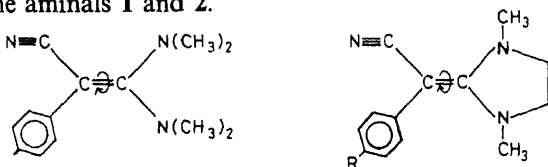
Recently, more rigorous statistical mechanical simulation techniques of treating liquids theoretically have been developed. These are the methods of molecular dynamics and Monte-Carlo statistical mechanics, and have been successfully applied to pure liquids and several solute-solvent systems (Rebertus *et al* 1979; Jorgensen 1981; Clementi and Corongiu 1980), though their requirement of extensive computation is preventing their more common usage.

4.1 Non-specific medium effect

Examples of a non-specific medium effect may be found in solutions of some of the substituted ethanes and ethylenes. The effect of solvent polarity on the conformational preferences in substituted ethanes has been discussed in detail and quantitatively by Abraham and coworkers (Abraham *et al* 1966; Abraham and Cooper 1967; Abraham *et al* 1974; Abraham and Bretschneider 1974) based on the reaction field concept. The results of these studies revealed that the ground state energies of more polar isomers are stabilized to a greater extent in polar media as compared to that in the gas phase or in non-polar solvents. For example, ΔE_{gt} ($= E_{\text{gauche}} - E_{\text{trans}}$) for 1,2-dichloroethane (DCE) has been shown, on the basis of the reaction field theory, to be reduced from 5.0 kJ mol^{-1} (Lowe 1968) in vapour to 1.8 kJ mol^{-1} (obs. 1.3 kJ mol^{-1}) in pure liquid, and to 0.5 kJ mol^{-1} (obs. 0.6 kJ mol^{-1}) in acetonitrile (Abraham and Bretschneider 1974), due to the relative stabilization of the more polar gauche form in polar media (figure 13).

The same molecule, DCE, has been studied by means of Monte-Carlo calculations by Jorgensen (Jorgensen 1981; Jorgensen *et al* 1981). Similar to the results of Abraham and Bretschneider, he found the gauche population of DCE to be increased drastically in the liquid state, as compared to the gas phase, as shown in figure 14. Even in systems which are generally considered to be non-polar, *e.g.* liquid *n*-butane (Jorgensen *et al* 1981) and *n*-butane in CCl_4 (Rebertus *et al* 1979), qualitatively, the same results were obtained, though the size of the medium effect was naturally much smaller. As is apparent from these examples, the stabilization energy on rotamers of substituted ethanes due to a medium effect is usually of the order of a few kJ mol^{-1} . Since the energy differences between conformational isomers are of the same order of magnitude, the medium can have a determining effect on the isomer populations.

The barrier to internal rotation, on the other hand, is determined by the difference between the energies of the ground state and the transition state. Each state may be affected by molecular interactions to a different degree. If the transition state is more polar than the ground state, and if it is assumed that molecules in the transition state may be treated in a manner similar to the treatment of the ground states, then the energy barrier to rotation should be reduced in polar media. Such an effect has indeed been observed by Kalinowski *et al* (1974) in the internal rotation about the CC double bond in the ketene aminals **1** and **2**.



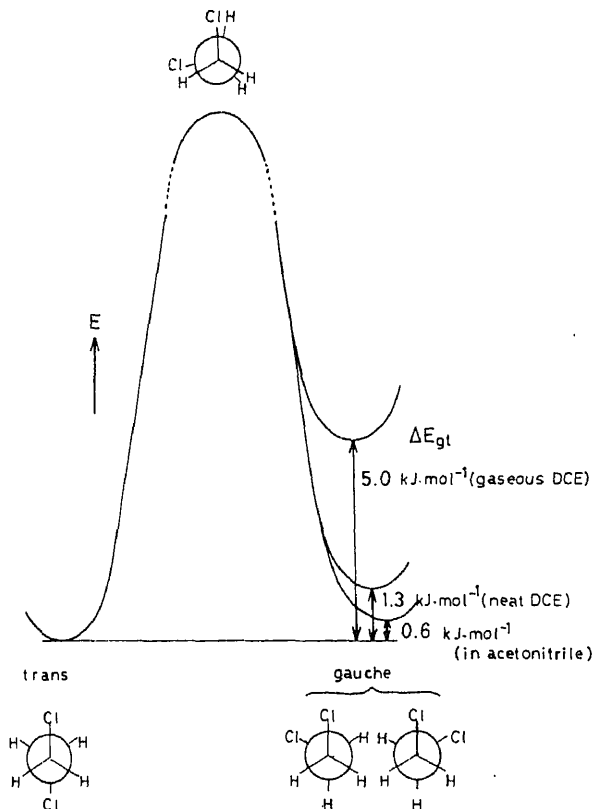
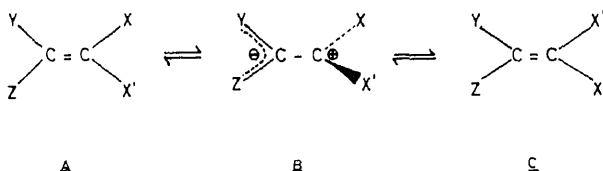


Figure 13. Schematic diagram showing the relative stabilization of the *gauche* conformation of dichloroethane (DCE) in liquid states with respect to that in the gaseous state.

The rotation about the CC double bond in these molecules takes place *via* the transition state **B**. When the free energy of activation is plotted against the solvent polarity, the following relationship is observed:



polarity in terms of the E_T factor, an approximately linear correlation, within experimental errors, has been obtained and $\Delta G^\ddagger$ has been found to *decrease* in the more polar solvents, as illustrated in figure 15. Since the solvents employed in this case were mostly aromatic, the possibility of π -complex formation cannot be denied completely. However, the rough linearity with the E_T factor indicates the polarity of the medium is the primary factor in the stabilization of the transition state.

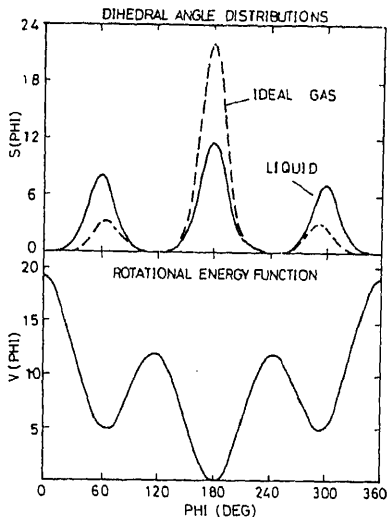


Figure 14 Upper: Computed population distributions for the dihedral angle about the CC bond in dichloroethane (DCE). Lower: Potential function (kJ mol^{-1}) for rotation about the CC bond in DCE. Units for $s(\phi)$ are mole fraction per degree $\times 10^{-3}$. Reprinted with permission from Jorgensen *et al* (1981). Copyright (1981) American Chemical Society.

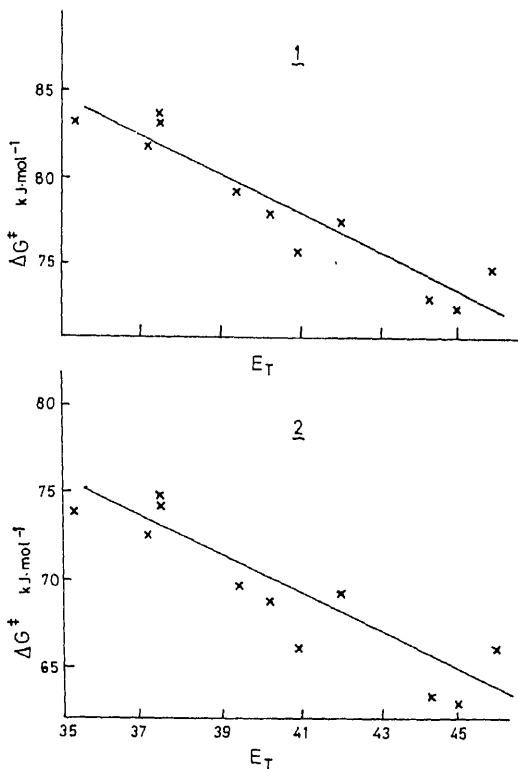


Figure 15 Free energy of activation of ketene epoxides 1 and 2 (see text) obtained by the

the ground state to be the twisted polar form, with the non-polar planar form being the transition state. As a result, the ground and transition states of **3A** have opposite polarities to those of **3B** and **3C**, respectively. The free energies of activation, $\Delta G^\ddagger$, were obtained in two solvents of different polarities, and tabulated in table 24. Though the size of the effect is small, it is seen that the ground state, and not the transition state, is more stabilized in **3B**.

In the series of compounds **3**, mentioned above, and the related series **4**, it was observed that activation entropies make a large contribution to $\Delta G^\ddagger$, and that the contribution is in opposite directions depending on the polarity of the transition state. The compounds of type **A** demonstrate large *negative* $\Delta S^\ddagger$ values, while those of type **B** and **C** give substantial *positive* $\Delta S^\ddagger$ values, as shown in table 25 (Berg and Sjöstrand 1978).

Table 24. Dependence of free energies of activation on the polarity of medium (Berg and Sjöstrand 1978).

Compound ^a	Solvent	Conc. (M)	ϵ^b	$\Delta G^\ddagger$ (kJ mol ⁻¹)
3A	<i>o</i> -C ₆ H ₄ Cl ₂	0.3	9.9	76.2
	C ₆ H ₅ CN	0.3	25.2	72.8
3B	<i>o</i> -C ₆ H ₄ Cl ₂	0.3	9.9	69.1
	C ₆ H ₅ CN	0.3	25.2	69.9

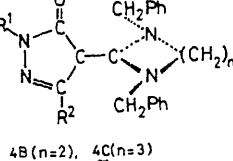
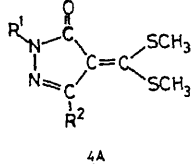
a. See text.

b. ϵ = dielectric constant of solvent.

Table 25. Activation parameters to internal rotation in substituted ethylenes, **3** and **4** (see text) (from Berg and Sjöstrand 1978)^a.

Compound	R ₁	R ₂	Solvent	T (K)	$\Delta G^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
3A			ODC ^b	365.3	77.4	49.6	-79.5
3B			ODC	332.3	69.5	80.3	+32.2
3C			ODC	433.6	92.1	110.5	+42.7
4A	Me	Me	C ₆ H ₅ CN	403.0 ^c	90.0	67.9	-44.4
4B	Me	Me	ODC	313.7	67.0		
4A	Me	Ph	ODC	383.1	78.4	55.5	-62.0
4B	Me	Ph	ODC-CDCl ₃ (1:1)	338.4 ^d	75.6		
4C	Me	Ph	ODC	455.2	95.4	107.6	+27.7
4A	Ph	Me	ODC	358.3 ^c	78.7		
4B	Ph	Me	CDCl ₃	319.8	68.2		
4A	Ph	Ph	ODC	328.1 ^c	67.8		
4B	Ph	Ph	ODC	365.7	76.6		
4C	Ph	Ph	ODC	459.2	99.2 ^d		

a. $\Delta G^\ddagger$ and $\Delta H^\ddagger$ are in kJ mol⁻¹; $\Delta S^\ddagger$ in J mol⁻¹ K⁻¹, measured at 100 MHz if not otherwise stated.



Difficulty in obtaining accurate values of entropy of activation has been repeatedly stressed. Enthalpy $\Delta H^\ddagger$ and entropy $\Delta S^\ddagger$ of activation are usually estimated from linear plots of $\ln k/T$ versus $1/T$ based on the Eyring rate equation,

$$k = \kappa \frac{kT}{h} \exp(-\Delta H^\ddagger/RT) \exp(\Delta S^\ddagger/R)$$

where κ is the transmission coefficient, k and h are Boltzmann's and Planck's constants, respectively, and the two parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, have quite often been observed to be linearly correlated. There are some chemical grounds for this linearity; a strong solute-solvent interaction, for example, will stabilize the system reducing its enthalpy, but at the same time, it will restrict the freedom of molecules and thus will result in a smaller entropy value. According to detailed discussions given by Krug *et al* (1976a, b), however, the main origin of the generally observed linearity is not necessarily due to such chemical phenomenon, but is often due to the fact that the errors in the enthalpy estimates are highly correlated with errors in the entropy estimates.

Binsch and his group (Höfner *et al* 1978a, b) studied activation entropies in detail. The factors which contribute to the total activation entropy are the vibrational, rotational and translational partition functions as well as the entropy of mixing of isomeric species of equal energy. Based on very precise DNMR studies on complex and strongly coupled spin systems, and also on the same principles of statistical mechanics for both the ground states and the transition state, they estimated the possible values of each contribution to $\Delta S^\ddagger$. Although the precision of their estimation still remains to be improved, they found no unrationalizable contributions to $\Delta S^\ddagger$. For their system of investigation, that is, the ring reversal of cyclohexane, they found the activation entropy $\Delta S^\ddagger$ to be small. They also expressed doubts about the possibility of finding large contributions to $\Delta S^\ddagger$ from solvent effect in 'non-ionic and non-associated organic molecules in non-hydroxylic organic solvents' (Höfner *et al* 1978b). This is in accord with the assumption adopted in general that the activation entropies are negligible for intramolecular processes and a large value of $\Delta S^\ddagger$ is usually caused by systematic errors, or by the effect of molecular associations.

It does not seem likely, however, that the observed large values of $\Delta S^\ddagger$ in the substituted ethylenes, **3** and **4**, above (table 25; Berg and Sjöstrand 1978) are entirely artifacts due to systematic errors. The sign of $\Delta S^\ddagger$ strikingly well corresponds with the differences in the polarities of the ground and transition states of the two types of molecules, **A** with respect to **B** and **C**. If the vibrational and/or rotational freedom of the side groups constituted the major contribution to the entropy, then the above effect should be reversed; $\Delta S^\ddagger$ would more likely be positive for the molecules of type **A** and negative for types **B** and **C**. It may be concluded, therefore, that the entropy effect in this case is caused by solvent-solute associations. Berg and Sjöstrand (1978) thus interpreted the result, stating that the polar form of a solute molecule will polarize the surrounding medium so that the solvent molecules in the immediate vicinity of the

solute will be 'immobilized' or have a smaller entropy. If the transition state is the polar form, then the system will show a negative entropy of activation and *vice versa*. There are also reported cases where the entropy term makes the major contribution to the overall stabilities of the conformational isomers (Wang and Bushweller 1977).

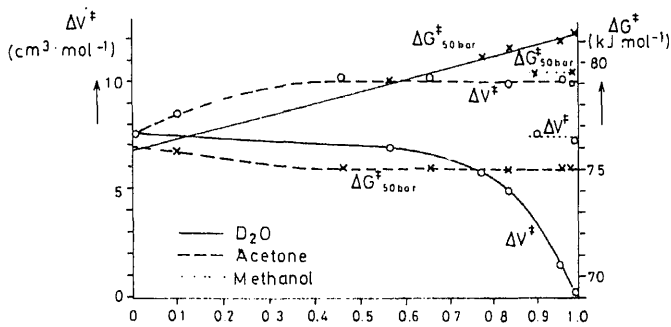
These examples suggest that entropy information will provide more detailed knowledge about the internal rotations and intermolecular interactions than will the free energy of activation, in which the major contribution from molecular interactions may have been cancelled out. At present, however, due to the lack of accurate measurements of $\Delta S^\ddagger$, we have to be contented with interpretations in terms of $\Delta G^\ddagger$, which are considered to be relatively accurate.

Another parameter which is suggested as providing a similar type of information as does entropy on the molecular interaction is the volume of activation, $\Delta V^\ddagger$. In case of internal rotation, it is the volume change of the system associated with rotational activation of molecules and is defined by

$$(\partial \ln k / \partial p)_T = -\Delta V^\ddagger / RT.$$

It is determined by the pressure-dependence of the rotational rate k at a constant temperature in the vicinity of T_c , the coalescence temperature, where the spectra are most sensitive to variations in k . Lüdemann and his group (Lüdemann *et al* 1977; Rauchschwalbe *et al* 1978; Völkel *et al* 1979; Hauer *et al* 1980) have studied the activation volumes for the C–N bond rotation in several N,N-dialkylamides and primary amides. The influence of the solvent polarity upon the activation volume and on the free energy of activation was determined in a wide variety of solvents, including CCl_4 , C_6D_6 , $(\text{CD}_3)_2\text{CO}$, $(\text{CD}_3)_2\text{SO}$, CD_3CN , CD_3OD and D_2O . In all solvents, $\Delta V^\ddagger$ was found to be surprisingly constant, at around $10 \text{ cm}^3 \text{ mol}^{-1}$ for N,N-dialkylamides and $2\text{--}3 \text{ cm}^3 \text{ mol}^{-1}$ for primary amides, and to be independent of the amide concentration. Only for aqueous solutions of N,N-dialkylamides particularly in very dilute regions did they find significantly lower $\Delta G^\ddagger$ values (figure 17).

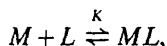
Two interpretations of their result have been suggested. Asano and le Noble (1978) in their review suggested that the positive $\Delta V^\ddagger$ of about $10 \text{ cm}^3 \text{ mol}^{-1}$ is the result of loss of the resonance-induced dipole by the rotating amide upon activation. The relatively



non-polar transition state would have a weaker amide-solvent interaction compared to the polar ground states and lead to the positive $\Delta V^\ddagger$ observed. Lüdemann *et al* (1977) contested that the activation volume is mainly determined by the intramolecular factors, i.e. the steric requirements of the rotating group rather than the inter-molecular contributions in this case and suggested that the small values of $\Delta V^\ddagger$ found in primary amides confirms the dominance of steric effects. They also suggest that amide molecules are not distributed uniformly in solutions, but tend to self-associate, the only exception being in aqueous solution at very high dilution. The monomeric amide then carries, on the time average, an open hydration shell which permits the rotation of the dimethylamino group without significant rearrangement of its immediate neighbourhood. When this hydration shell was disturbed by the addition of a small amount of sodium bromide or urea, a sharp increase of $\Delta V^\ddagger$ was observed (Völkel *et al* 1978).

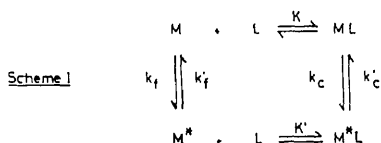
4.2 Specific intermolecular interactions

In this section, we consider those interactions which are more conveniently treated in terms of intermolecular associations at specific sites of molecules. They include hydrogen bonding, protonation, ionic interactions and complex formations. In these systems, free and interacting (complexed) species exist in equilibrium; the equilibrium constant for a 1:1 complex is



where L may be a hydrogen bonding donor or acceptor, an acidic proton, an ion, or a complexing reagent. In addition to this basic equilibrium, the system may also be comprised of additional equilibria such as formation of higher order complexes, self-association of any of the species involved, complexation at a different site to form another complex (ML'), active involvement of a third component such as solvent molecules, etc.

Inclusion of the internal rotation in the above basic equilibrium leads to the following reaction scheme;



where M^* denotes the rotational isomer of molecule M , and k_f 's and k_c 's are the rate constants for the internal rotation of free and complexed molecules, respectively. If association and dissociation process takes place sufficiently rapidly, the observed rate of internal rotation of M will be the weighted average of the rotational rates in M and ML (Trotter *et al* 1973; Cheng and Gutowsky 1980);

$$k_{\text{obsd}} = x_f k_f + x_c k_c,$$

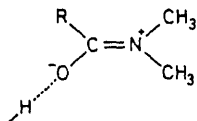
where x_f and x_c represent the mole fractions of the free and complexed molecules, respectively. The observed free energy of activation, $\Delta G^\ddagger$, is then given by the following expression,

A mechanism similar to scheme I will apply to almost all dynamic systems which are simultaneously involved in molecular interaction equilibria. For a complete analysis of the system, the above equations should be solved for all the x and k (or $\Delta G^\ddagger$) values based on the chemical shifts and ^1H NMR data measured at different resonance frequencies (and temperatures) and with different concentrations (Cheng and Gutowsky 1980), though the complete analysis could be quite time-consuming.

4.2a. *Hydrogen bonding*: As already mentioned, many types of associations are possible for amides in solutions depending on the types of amides and the solvents. N,N -dialkylamides and -thioamides are known to exist as self-associated dimers, neat or in concentrated solutions in non-interacting solvents. In dipolar aprotic solvents, they are presumably associated with solvent molecules by dipole-dipole association, in addition to self-association, and in protic solvents, hydrogen bonding to the carbonyl group must also be present. Because of the presence of many interaction equilibria of similar K values, the dynamics of these systems are complex and have not been treated very quantitatively.

The magnitude of the effect of these various molecular associations on the amide rotational barriers could be discussed more quantitatively if the data on the monomeric species were available. ^1H NMR studies on gaseous amides have been extremely scarce, even with the recent technical improvement in NMR spectrometers. It is rather fortunate, therefore, that we have a few such measurements available for amides, dimethylacetamide (DMA) (Feigel 1980), dimethylthioformamide (DMTF) (Drakenberg 1976b), and dimethyltrifluoroacetamide (Ross *et al* 1983) as references for comparison. They are listed in table 26, together with the data observed in various solutions.

From the table, it is apparent that the $\Delta G^\ddagger$ values are, when compared with the gas phase value, considerably higher even in fairly non-polar solvents at low amide concentrations. It is likely that the $\Delta G^\ddagger$ values of DMA found in CCl_4 and isooctane, for example, are in fact weighted means for the monomer $\rightleftharpoons$ dimer equilibrium existent in those solutions, and not the values for purely monomeric species. On the other hand, the $\Delta G^\ddagger$ value obtained in pure liquid (neat) likely represents the activation free energy for the dimeric species, and that found in dipolar solvents should correspond to amides associated with solvent molecules by means of dipolar interactions. Since DMA is a highly dipolar liquid itself, the similarity of $\Delta G^\ddagger$ values, neat and for DMSO solution is reasonable and the increase of $10\text{--}12\text{ kJ mol}^{-1}$ in $\Delta G^\ddagger$ over the gas phase value should represent mainly the increase due to stabilization of the dipolar ground state by dipolar association. Hydrogen bonding to the carbonyl group of amides seems to increase the barrier further, by about 16 kJ mol^{-1} or more in case of DMA in formamide and D_2O compared with the corresponding gas phase value. This is a reasonable increase if the stabilization of the ground state of amides due to hydrogen bonding through the carbonyl is considered.



Unlike N,N -dialkylamides, primary and secondary amides interact primarily by hydrogen bonding through the N-H protons as well as the carbonyl group. The

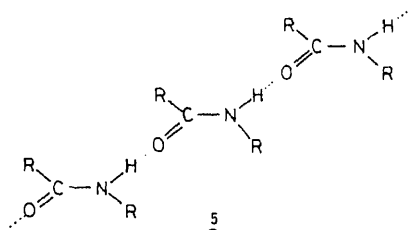
Table 26. Medium dependence of barriers to internal rotation in some dimethylamides.

Solvent	Conc. (mol %)	E_a (kJ/mol)	$\Delta G^\ddagger_{198}$ (kJ/mol)	$\Delta S^\ddagger$ (J/mol/K)	Refer
<i>N,N</i> -Dimethylacetamide (DMA)					
Gas (acetone- d_6 gas added)			65.5		1
CCl_4	1.7	76.6	72.8	4.6	2
Isooctane	2.6	75.3	72.4	2.1	2
Neat	100	82.0	76.1	12.1	3
DMSO- d_6	9.5	84.9	77.4	17.2	4
Formamide	9.8	89.1	81.2	18.4	3
D_2O	2.0	87.9	81.6	12.6	5
<i>N,N</i> -Dimethylthioformamide (DMTF)					
Gas (TMS gas added)			94.1		6
Decalin	0.1		98.3		6
<i>m</i> -DCB	0.01		101.3		6
	0.1		102.9		6
	1		103.8		6
Neat			106.7		6
<i>N,N</i> -Dimethyltrifluoroacetamide					
Gas (1 torr/103 torr Ar)		68.6	67.4	-4.6	7
CCl_4	10%	74.5	73.6	-2.5	7

References: 1. Feigl (1980); 2. Neuman and Jonas (1974b); 3. Neuman *et al* (1974); 4. Neuman and Jonas (1971); 5. Temussi *et al* (1969); 6. Drakenberg (1976b); 7. Rossmoore *et al* (1983).

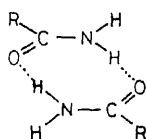
and Pullman 1970; Dreyfus *et al* 1970; Johansson *et al* 1974; Del Bene 1978) seem to agree that the stabilization brought about by hydrogen bond formation in the linear formamide dimer is about 40 kJ mol^{-1} ; cyclic formamide dimer, 60 kJ mol^{-1} ; formamide- H_2O , $25\text{--}27 \text{ kJ mol}^{-1}$, with approximately the same amount of stabilization gained whether the amide is acting as a hydrogen bond donor or as an acceptor (Del Bene 1978).

The effect of methyl substitution on the hydrogen-bonding ability of amides has been studied using the amide-water system as the model (Johansson and Kollman 1974; Johansson *et al* 1974; Del Bene 1978). The results have revealed that methyl substitution either at nitrogen or at the carbonyl carbon has a destabilizing effect on the strength of amide-water hydrogen bonding when amide is acting as a proton donor (N-H ... OH₂). On the other hand, the ability as a proton acceptor at the carbonyl carbon (C=O ... H-OH) will be strengthened by methylation at the carbonyl carbon by ca 1.8 kJ mol^{-1} (acetamide-water vs formamide-water pair), while the effect is much smaller when the methylation is at the nitrogen, by ca 0.4 kJ mol^{-1} (N-methylformamide-water vs formamide-water pair) (Del Bene 1978).

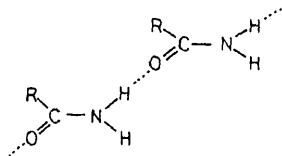


the nitrogen proton (Graham and Chang 1971b). Thus, they are found to be approximately equally effective in disrupting interamide hydrogen bonds.

Primary amides have two N-H protons available for hydrogen bonding, in addition to the carbonyl oxygen. Molecular orbital calculations showed that the cyclic type **6A** is much more stable than the linear type **6B** for the self-association of primary amides.



6A



6B

Indeed, when solvent molecules are unable to form hydrogen bonds to the amide protons, such as in chloroform, only amide monomer $\rightleftharpoons$ cyclic dimer equilibrium seems to exist in the solution, and dissociation of cyclic dimer becomes appreciable only at concentrations of amide as low as 10^{-3} mole fractions, as judged from the concentration dependence of the two amide proton chemical shifts of mono-fluoroacetamide in chloroform (Handa and Umemoto 1981).

In aprotic solvents, on the other hand, it is customary to find both amide protons showing a large concentration dependence, indicating that both protons are involved in associations. Even in such solvents, amide cyclic dimer of the form **6A** seems to become important as the amide concentration is increased (Umemoto and Ouchi 1981). It is also evident from the chemical shift dependence on concentration, that self-association and/or amide-solvent interaction are always present in solutions of primary amides even at the lowest amide concentration attainable for NMR observations. It is not surprising, therefore, that information on the barriers to internal rotation of primary amides in their monomeric state is not available; all the data listed in table 27 are obtained for amides either self-associated, associated to solvent molecules through hydrogen bonding, or more commonly in a mixture of both. For the same reason, it is reasonable in primary amides to find a rather small dependence of $\Delta G^\ddagger$ on solvents, even smaller than the dependence found in N,N-disubstituted amides which form various types of interactions depending on the type of solvent. In table 27, it is still observable that the polarity of the medium seems to affect the $\Delta G^\ddagger$ values slightly, with more polar ground state and thus increasing the barrier.

The ability of solvent to form hydrogen bonds sometimes produces a large effect on the barrier to rotation in systems involving intramolecular hydrogen bonding. N,N-dimethyl-2-hydroxy-4-methoxythiobenzamide **7**, takes part in intramolecular

Table 27. Solvent dependence of activation parameters for internal rotation in acetamide^a.

Solvent ^b	ϵ^c	Conc.	$\Delta G_{298}^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
1,4-Dioxane	2.2	5.7 m % ^d	70.1	85.6	52	1
1,3-Dioxane		5.8 m %	70.0	78.9	30	1
Acetone	20.7	0.5 M	69.9	76.1	21	2
Methylpropylketone		5.9 m %	70.1	80.8	36	1
		9.0 m %	70.4	80.8	35	1
		12.0 m %	70.5	77.5	24	1
DMF	36.7	1.5 M	72.4	84.1	38	2
DMSO	48.9	6.0 m %	72.7	78.3	19	1

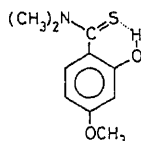
a. $\Delta G^\ddagger$ and $\Delta H^\ddagger$ are in kJ mol^{-1} ; $\Delta S^\ddagger$ in $\text{J mol}^{-1} \text{K}^{-1}$.

b. DMF = N,N-Dimethylformamide; DMSO = dimethylsulfoxide.

c. ϵ = dielectric constant of solvent.

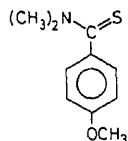
d. m % = percent mole fractions.

References: 1. Umemoto and Ouchi (1981); 2. Drakenberg (1972).



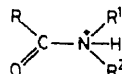
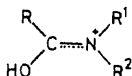
7

CDCl_3 and pyridine- d_5 , and found an increase in $\Delta G^\ddagger$ of 8 kJ mol^{-1} in the solvent. This drastic increase of $\Delta G^\ddagger$ in pyridine has been interpreted as indicating pyridine effectively competes with the thiocarbonyl group to disrupt the intramolecular hydrogen bond, increasing $\Delta G^\ddagger$ to a value closer to that of **8**.



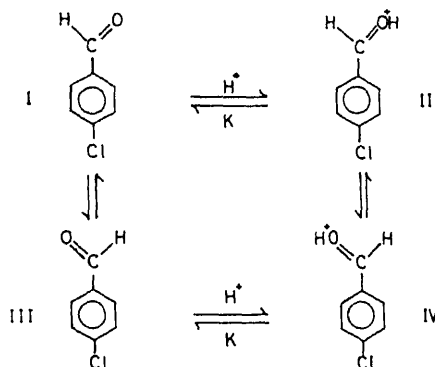
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4.2b. *Protonation:* Protonation produces two opposite effects on the barrier to rotation in amides depending on the protonation site. O-protonation (**I**) will raise the barrier to rotation, while N-protonation (**II**) will result in an almost free rotation, as indicated by the structures **I** and **II**. Both types of protonation are detected in a solution, with O-protonation (**I**) being predominant under strongly acidic conditions. A small amount of N-protonated species **II**, however, effectively lowers the barrier to rotation.



more weakly acidic media, playing a role as an intermediate to proton exchange in the cases of primary and secondary amides (Jackman 1975; and references therein).

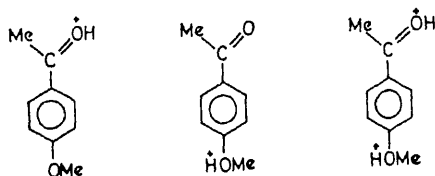
The interpretation of the effect of protonation on rotational processes, therefore, requires detailed knowledge of equilibria and rate processes present in the system. Drakenberg *et al* (1974b) studied by means of both ^1H and ^{13}C complete bandshape analysis the system of protonated *p*-chlorobenzaldehyde **9** in 'superacid' medium ($\text{FSO}_3\text{F}-\text{SbF}_5$ 1:1). Protonation at the carbonyl oxygen as in **II** and **IV** increases the



barrier because of the subsequent increase in the double bond character in the Ph-carbonyl bond. Detailed DNMR bandshape analysis has revealed that although the $\text{II} \rightleftharpoons \text{IV}$ process is predominant and the relative population of unprotonated species (**I** and **III**) is very small ($< 10^{-3}$), the protonation-deprotonation process makes a large effect on the overall exchange rate and thus on the result of bandshape analysis. They point out that the relative populations of **I** and **III** have to be less than 10^{-6} in order that the involvement of these species may safely be neglected in the bandshape analysis.

A number of other protonated aromatic aldehydes and ketones have been investigated by DNMR and some of the data has been listed earlier (§3.1, table 6). The free energy of activation about the Ph-carbonyl bond is seen to increase drastically upon protonation, and the inductive and resonance effect of the *para*-substituent on $\Delta G^\ddagger$ are amplified accordingly.

Para-methoxyacetophenone **10** has another site of protonation at the methoxy oxygen (as in **B**) which, in contrast to the first protonation site (**A**), will decrease the rotational energy barrier. Barthelemy *et al* (1978) performed a complete bandshape analysis to obtain $\Delta G^\ddagger$ for the internal rotation of **10** in a series of acidic solvents ranging from $\text{FSO}_3\text{H}-\text{SbF}_5$ ($H_0 \cong -25$) to FSO_3H containing 30% base



($\eta_0 \approx -10$). The results obtained are tabulated in table 28. When the medium is more acidic than pure FSO_3H , the observed $\Delta G^\ddagger$ values correspond well to the values expected for diprotonated species C. When the medium is less acidic than FSO_3H , the observed $\Delta G^\ddagger$ is independent of the acidity of the solvent indicating that only the mono-protonated species A is present. However, the observed $\Delta G^\ddagger$ is about 6 kJ mol^{-1} smaller than the value expected from $\Delta G^\ddagger$ vs σ^+ correlations. This discrepancy has been attributed to the presence of a small amount of the methoxy protonated species B. An amount as small as 10^{-8} mole fraction was sufficient to account for the observed discrepancy (Barthelemy *et al* 1978).

4.2c. *Interaction with electrolytes:* Amides also strongly interact with various electrolytes. In particular, the interactions of metal cations with amides have been the subject of considerable interest because of biological implications in relation to the dynamics of proteins. Molecular orbital calculations (Gupta and Rao 1973; Rode and Fussenegger 1975; Hinton *et al* 1977; Corongiu *et al* 1980) indicate that Li^+ ions bind preferentially to the carbonyl oxygen of amides, stabilizing the polar ground state and increasing the C-N bond order. As a result, the barrier to rotation around the C-N bond is expected to increase. Such an increase in the barrier upon the addition of Li^+ in neat DMF was indeed observed experimentally as shown in table 29.

Waghorne *et al* (1980) examined by means of complete bandshape analysis, the system of DMA and various mono- and divalent metal cations in a non-aqueous media, propylene carbonate, the results being included in table 29. As they have pointed out, the results are most likely weighted averages of the rates of internal rotation of the complexed and uncomplexed amide molecules for the scheme I-type system. The results indicate that interaction of the amides with alkali cations and such divalent

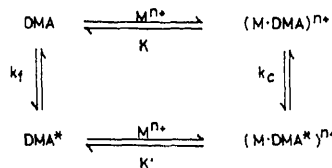


Table 28. Dependence of $\Delta G^\ddagger$ of rotation around the phenyl-CO bond in *p*-methoxyacetophenone on the acidity of solvents (Berthelemy *et al* 1978).

% SbF_5 in $\text{HSO}_3\text{F}/\text{SbF}_5$	H_0	$\Delta G^\ddagger$ (kJ mol^{-1})
50	< -21	41.4
8	-18.7	42.7
2	-17.6	42.5
1	-17.3	43.0
% Base in HSO_3F	H_0	$\Delta G^\ddagger$ (kJ mol^{-1})
1	-14.2	55.1
2	-14.05	55.5
5	> -13.0	55.2
20		54.8
30		55.0

Table 29. Activation parameters for C–N bond rotation in some amide-cation systems.

System	Ratio	E_a (kJ mol ⁻¹)	Reference
DMF-d		90.4	1
DMF-d : LiCl	4 : 1	104.6	1
DMA		76.6	2
DMA : LiClO ₄	1 : 0.48	75.3	2
	1 : 0.96	79.5	2
	1 : 1.62	81.2	2
	1 : 3.85	84.5	2
	1 : 9.35	84.1	2
DMA : LiBr	1 : 0.64	82.8	2
DMA : NaClO ₄	1 : 9.56	79.5	2
DMA : Pb(ClO ₄) ₂	1 : 1.00	80.3	2
	1 : 2.00	81.2	2
DMA : Zn(ClO ₄) ₂	1 : 2.00	81.6	2
DMA : Cd(ClO ₄) ₂	1 : 2.00	83.3	2
DMA : Mg(ClO ₄) ₂	1 : 2.00	88.3	2
DMA : AgClO ₄	1 : 0.55	70.3	2
	1 : 0.88	70.3	2
	1 : 1.97	69.5	2
	1 : 4.06	69.5	2

References: 1. Rao *et al* (1977); 2. Waghorne *et al* (1980).

cations as Pb²⁺, Zn²⁺, Cd²⁺ and Mg²⁺ increases the barrier to C–N bond rotation of DMA by several kJ mol⁻¹ or more as compared to the case of uncomplexed DMA. For a more quantitative estimate of the barrier of each complex, however, a complete equilibrium-kinetics treatment is required.

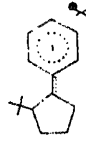
The unique behaviour of the Ag⁺ complex, that is, the lowering of activation energy upon complexation, appears in the results given in table 29 and also has previously been reported. It has been attributed to a small but kinetically significant amount of the N-complexed species as in the case of protonated amides (Temussi and Quadrifoglio 1968; Temussi *et al* 1969), though the precise exchange mechanism of the silver-amide complex is not fully understood.

Effects of ionic interactions on internal rotation have been investigated in a number of delocalized carbanions and -cations by ¹H and ¹³C DNMR. These systems have attracted considerable interest since the barriers to rotation may provide a direct measure of the extent of delocalized π -bonding, in addition to some detailed information concerning ionic and solvent interactions in the system. Typical of these systems are allyl anions and arylmethyl ions, some of their DNMR results being summarized in table 30.

Increased barriers to rotation depending on the counter-ions in the order Li⁺ < Na⁺ < K⁺ < Cs⁺ have generally been observed in these systems. Such an effect is evidently demonstrated in the table for the allyl anion (**11**; R₁ = R₂ = R₃ = H) and naphthylmethylanions (**15** and **16**), and has been discussed in terms of the solvent-separated ion pair $\rightleftharpoons$ contact ion pair equilibrium, which is shifted to the right for larger cations (Thompson and Ford 1979 and references therein). In fact, contact ion pairs are

Table 30. Barriers to internal rotation in carbanions and -cations^a.

No.	Compound	$\underline{R}_1$	$\underline{R}_2$	$\underline{R}_3$	Counter ion (X)	Solvent	RB ^b	$\Delta G^\ddagger$ (T)	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
11. Allyl anions											
		H	H	H	Li ⁺	THF-d ₈		44.8 (222)			1
					K ⁺	THF-d ₈		69.9 (341)			1
		H	Me		Cs ⁺	THF-d ₈		75.3 (341)			1
		Me	H	H	K ⁺	THF-d ₈		66.5 (325)			1
					K ⁺	THF-d ₈		75-92			1
							C ₁ -C ₂	71.1 (341)			1
							C ₂ -C ₃	> 80.8 (341)			1
	(Z)	Pr ⁱ	H	H	K ⁺	THF-d ₈		71.1 (320)			1
	(E)	Pr ⁱ	H	H	K ⁺	THF-d ₈		58.6 (301)			1
		Ph	H	Ph	Li ⁺			45.6 (233)			2
Diphenylallylanions											
		Ph	H	Ph	Na ⁺	c					
		Ph	CN	Ph	K ⁺	DMSO		69.0 (335)	52.3	-50	3
		bp ^j	H	bp ^j	Na ⁺	THF-d ₈		57 (298)			4
		Ph	H	Ph	Li ⁺	THF-d ₈		56 (298)			4
12.											
13. Benzyl anions											
		Me	np ^d	H	Li ⁺	TME/IO ^e		77.8 (298)	78.2	1	5
		Me	np	Pr ⁱ	Li ⁺	TME/IO		71.5 (298)	77.4	19	5
		Me	np	Bu ^t	Li ⁺	TME/IO		71.1 (298)	77.4	22	5
		Me	np	GeMe ₃	Li ⁺	TME/IO			76.1	20	6
		Me	np	SiMe ₃	Li ⁺	TME/IO			92.0	14	6
		Me	np	cp ^f	Li ⁺	TME/IO			49.4	-65	6
		Me	np	Ph	Li ⁺	TME/IO			> 109		6
		Me	np	SPh	Li ⁺	TME/IO			> 109		6
		Me	np	SiMe ₂ Ph	Li ⁺	TME/IO			> 109		6

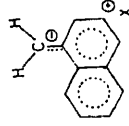


14.

64.4
49.8

-22
-42

15. 1-Naphthylmethyl anion



55.6
63.6
76.1

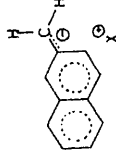
6
6
7

54.0
61.9
74.4

THF-d₈
THF-d₈
THF-d₈

Li⁺
Na⁺
K⁺

16. 2-Naphthylmethyl anion



53.6
74.5

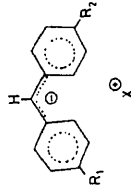
1
48

53.6
61.1

THF-d₈
THF-d₈

Li⁺
Na⁺

17. 1,3-Diphenylmethyl anions



H

H

H

H

H

H

H

H

H

THF
HMPA/THF
HMPA/THF
/18-c-6^g
HMPA/THF

K⁺
K⁺
K⁺

H

H

H

H

H

H

H

H

H

45.6 (238)
50.2 (262)

C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃

THF
HMPA/THF
HMPA/THF
/18-c-6^g
HMPA/THF

K⁺
K⁺
K⁺

H

H

H

H

H

H

H

H

H

49.0 (238)
42.3 (219)
49.0 (223)
45.2 (223)
44.8 (232)
41.8 (250)
52.7 (250)

C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃

THF
HMPA/THF
HMPA/THF
/18-c-6^g
HMPA/THF

K⁺
K⁺
K⁺

H

H

H

H

H

H

H

H

H

50.6
46.9

C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃

THF
HMPA/THF
HMPA/THF
/18-c-6^g
HMPA/THF

K⁺
K⁺
K⁺

H

H

H

H

H

H

H

H

H

50.6
46.9

C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃

THF
HMPA/THF
HMPA/THF
/18-c-6^g
HMPA/THF

K⁺
K⁺
K⁺

H

H

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H

49.0 (238)
42.3 (219)
49.0 (223)
45.2 (223)
44.8 (232)
41.8 (250)
52.7 (250)

C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃

THF
HMPA/THF
HMPA/THF
/18-c-6^g
HMPA/THF

K⁺
K⁺
K⁺

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49.0 (238)
42.3 (219)
49.0 (223)
45.2 (223)
44.8 (232)
41.8 (250)
52.7 (250)

C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃

THF
HMPA/THF
HMPA/THF
/18-c-6^g
HMPA/THF

K⁺
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K⁺

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49.0 (238)
42.3 (219)
49.0 (223)
45.2 (223)
44.8 (232)
41.8 (250)
52.7 (250)

C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃

THF
HMPA/THF
HMPA/THF
/18-c-6^g
HMPA/THF

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C₁-C₂
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C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃

THF
HMPA/THF
HMPA/THF
/18-c-6^g
HMPA/THF

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41.8 (250)
52.7 (250)

C₁-C₂
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C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃

THF
HMPA/THF
HMPA/THF
/18-c-6^g
HMPA/THF

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49.0 (238)
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49.0 (223)
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44.8 (232)
41.8 (250)
52.7 (250)

C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃

THF
HMPA/THF
HMPA/THF
/18-c-6^g
HMPA/THF

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K⁺

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42.3 (219)
49.0 (223)
45.2 (223)
44.8 (232)
41.8 (250)
52.7 (250)

C₁-C₂
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C₁-C₂
C₂-C₃
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C₂-C₃

THF
HMPA/THF
HMPA/THF
/18-c-6^g
HMPA/THF

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49.0 (238)
42.3 (219)
49.0 (223)
45.2 (223)
44.8 (232)
41.8 (250)
52.7 (250)

C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃

THF
HMPA/THF
HMPA/THF
/18-c-6^g
HMPA/THF

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K⁺

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49.0 (238)
42.3 (219)
49.0 (223)
45.2 (223)
44.8 (232)
41.8 (250)
52.7 (250)

C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃

THF
HMPA/THF
HMPA/THF
/18-c-6^g
HMPA/THF

K⁺
K⁺
K⁺

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49.0 (238)
42.3 (219)
49.0 (223)
45.2 (223)
44.8 (232)
41.8 (250)
52.7 (250)

C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃

THF
HMPA/THF
HMPA/THF
/18-c-6^g
HMPA/THF

K⁺
K⁺
K⁺

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H

49.0 (238)
42.3 (219)
49.0 (223)
45.2 (223)
44.8 (232)
41.8 (250)
52.7 (250)

C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃
C₁-C₂
C₂-C₃

THF
HMPA/THF
HMPA/THF
/18-c-6^g
HMPA/THF

K⁺
K⁺
K⁺

H

H

H

H

Table 30. (Continued)

No.	Compound	Substituents		Counter ion (X)	Solvent	RB ^b	ΔG° (T)	ΔH°	ΔS°	Reference
		$\underline{R}_1$	$\underline{R}_2$							
19.				Li ⁺	NH ₃		63.2 (300)			10
20.		OMe		Li ⁺	NH ₃		> 71			11
		Me		K ⁺	NH ₃		> 71			11
		H		Li ⁺	NH ₃		68.6 (311)			11
		H		Li ⁺	HMPA		67.8 (304)			11
		H		Li ⁺	NH ₃		60.2 (277)			10
		H		K ⁺	NH ₃		63.2 (300)			11
		H		Li ⁺	NH ₃		51.0 (235)			11
21.				Li ⁺	NH ₃		68.6 (311)			11

a. ΔG° and ΔH° are in kJ mol^{-1} ; ΔS° in $\text{J mol}^{-1} \text{K}^{-1}$; T in Kelvin.

b. RB = rotating bond.

c. [²H₅]methyl *t*-butyl ether/liq. NH₃.

d. np = neopentyl.

e. TME/O = N,N,N',N'-tetramethylethylenediamine/isooctane.

f. cp = cyclopropyl.

g. 18-c-6 = 18-crown-6 ether.

h. T/THF = toluene/THF.

j. bis(2,2'-biphenylene).

References: 1. Thompson and Ford (1970); 2. R. L. ...

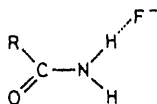
are found as the predominant type of ion pair association in most of the allyl and methylallyl anions **11** (Thompson and Ford 1979).

However, in a more extensively delocalized π -system, 1,3-diphenylallyl anions (**11**; $R_1 = R_3 = \text{phenyl}$, $R_2 = \text{H or CN}$), it was observed that not only the rotational energy barriers, but also the ^1H and ^{13}C chemical shifts as well as infrared absorption spectra were independent of counter-ions, Li^+ , Na^+ or K^+ (Bushby and Ferber 1976; Boche *et al* 1976). Therefore, it has been concluded that solvent-separated ion pairs are preferred in these systems.

When chelating agents such as HMPA (hexamethylphosphorotriamide) or 18-crown-6 ether are added to a system of carbanions and alkali methyl cations, it is expected that the chelating agent will complex preferentially with the latter, shifting the equilibrium towards a solvent-separated type of interaction. Olah and Watkins (1980) found, however, that, although the addition of 18-crown-6 ether to a solution of diphenylmethyl anion **17** to which HMPA had already been added increased its rotational barrier, the ^{13}C chemical shifts of the carbanion remained unaffected. Such an experimental result is best explained by a mechanism involving the contact-ion-paired transition state, with the ground state of **17** being largely solvent-separated ion pairs or free ions. A similar mechanism has been proposed for interpretation of the results obtained for the *tert*-benzyl lithium compound **13**, for which it is suggested that the transition state of **13** is stabilized by the development of partial covalency from benzyl carbon to lithium (Fraenkel *et al* 1973; Fraenkel and Geckle 1980). Such a picture was also found useful in interpreting the large discrepancy between the experimental and calculated energy barriers of rotation in allyllithium (Thompson and Ford 1979).

It is generally believed that the anion influence on NMR of N,N-dimethylamides is small (Lassigne and Baine 1971). However, differing behaviour of ^{13}C chemical shifts of carbonyl carbons of DMA has been observed in aqueous LiCl and LiClO_4 solutions of DMA (Adams *et al* 1975), suggesting that, in aqueous systems, an amide-solvent (water) interaction may be disturbed by the presence of anions, to a differing extent depending on the strength of the anion-solvent interaction.

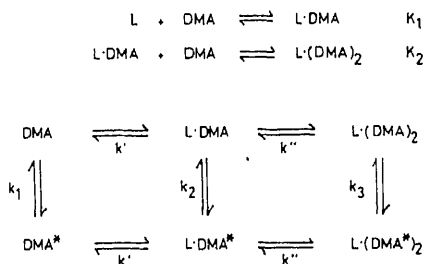
On the other hand, it is easily conceivable that primary and secondary amides interact strongly with anions. Exceptionally strong hydrogen bonding has been predicted for formamide- and acetamide-fluoride ion interactions, of the order of 147 kJ mol^{-1} , by an *ab initio* calculation (Emsley *et al* 1981). This would be the second strongest hydrogen bond known, second only to F-H-F^- . The optimal structure is found to be the one in which the fluoride ion is bonded to the N-H *trans* to the carbonyl



group. Such a hydrogen bond will effectively prevent the lone pair of electrons of the nitrogen atom from delocalizing into the amide's π -system, thereby decreasing the

However, there have been suspicions that the rate process may be influenced by the addition of LSR, contributing to the uncertainty in the barrier determinations. For amides, coordination of LSR usually occurs at the carbonyl group. According to Graham (1980), a preferred binding site of N,N-dimethylamides for $\text{Eu}(\text{fod})_3$ is on one of the lone-pair orbitals of the carbonyl oxygen atom, with a possible site of secondary binding on the other lone-pair orbital of the oxygen. A direct result of such coordination is a shift of the N-methyl protons *cis* to the carbonyl to low field by about twice as far as the *trans* protons.

Cheng and Gutowsky (1978, 1980) performed a detailed study of the effect of LSR on the kinetics of DMA, and obtained, by the coalescence-temperature method, the free energies of activation for the three species, DMA, $\text{L} \cdot \text{DMA}$, and $\text{L} \cdot (\text{DMA})_2$, where L is $\text{Pr}(\text{fod})_3$, which exist in 'two-step' equilibrium in tetrachloroethane:



where k' and k'' are the LSR-amide exchange rates and are in general fast on the NMR time scale, and k_1 , k_2 and k_3 are the rates of internal rotation of uncomplexed and complexed species. Though the LSR-amide exchange rates k' and k'' are much greater than the rotational process rate, their effects may not be neglected. The free energies of activation for the three species are;

DMA	76.9 kJ mol ⁻¹ ,
$\text{L} \cdot \text{DMA}$	81.6 kJ mol ⁻¹ ,
$\text{L} \cdot (\text{DMA})_2$	82.0 kJ mol ⁻¹ .

Therefore, it is apparent that the free energy of activation for internal rotation of DMA is increased by about 5 kJ mol⁻¹ upon complexation with $\text{Pr}(\text{fod})_3$ (Cheng and Gutowsky 1980). As illustrated in table 31, coordination to the carbonyl oxygen of amides by either LSR or Lewis acids generally increases the energy barrier. It is likely that such complexation at the carbonyl group leads to an increased double-bond character of the C-N bond and thus an increased barrier.

Kessler and Molter (1976) made a detailed investigation of the ^1H NMR of *tert*-butoxycarbonyl α -amino acid esters in the presence of $\text{Eu}(\text{fod})_3$. They found that with an increasing amount of LSR added to the solution, the population of the minor component, the E isomer increased, due probably to the preferential complexation and

Table 31. Effect of complex formation on barriers to internal rotation^a.

Compound	L ^b	Ratio ^c	Solvent ^d	RB ^e	$\Delta G^\ddagger$ (T)	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
MeCONMe ₂			Neat		75.7 (298)	76.6	3	1
	+ SbCl ₅	1:3	TCE		> 88 (408)			2
EtOCONMe ₂			CDCl ₃ /C ₆ D ₆		64.9 (298)	59.0	-19	2
	+ SbCl ₅	1:3	TCE		> 75 (330)			2
Me ₂ NCONHPr ⁱ			CH ₂ Cl ₂ /FT	C-NMe ₂	40.6 (298)	34.3	-18	3
	+ SbCl ₅	1:1	CD ₂ Cl ₂	C-NMe ₂	54.8 (298)	64.0	30	2
Me ₂ NCONH ₂			(CD ₃) ₂ CO	C-NMe ₂	44.5 (211)			4
	+ BF ₃		CH ₂ Cl ₂ /MeNO ₂	C-NMe ₂	65.2 (276)			5
Me ₂ NCONMe ₂			CH ₂ Cl ₂ /CHF ₂ Cl		26.4 (135)			6
	+ SbCl ₅		CH ₂ Cl ₂		50.1 (226)			7
MeHNCONHMe	+ BF ₃		CH ₂ Cl ₂ /MeNO ₂		66.9 (288)			5
EtHNCONHEt	+ BF ₃		CH ₂ Cl ₂ /MeNO ₂		65.2 (287)			5
Et ₂ NCONH ₂			(CD ₃) ₂ CO	C-NEt ₂	43 (205)			4
	+ BF ₃		CH ₂ Cl ₂ /MeNO ₂	C-NEt ₂	65.6 (287)			5
Me ₂ NCONEt ₂			CD ₂ Cl ₂	C-NMe ₂	< 33			4
	+ TiCl ₄		CD ₂ Cl ₂	C-NMe ₂	53.1			4
			CD ₂ Cl ₂	C-NEt ₂	< 33.4			4
	+ TiCl ₄		CD ₂ Cl ₂	C-NEt ₂	50.1 (253)			4

Table 31. (Continued)

Compound	L ^b	Ratio ^c	Solvent ^d	RB ^e	$\Delta G^\ddagger$ (T)	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
MeCONMe ₂			TCE		76.8 (346)			8
	+ Pr (fod) ₃	0.128	TCE		77.7			8
		0.192	TCE		77.9			8
		0.256	TCE		78.2			8
		0.384	TCE		79.0			8
		0.512	TCE		80.0			8
CH ₂ =CHCONMe ₂	+ Eu (fod) ₃	0.10	CDCl ₃		70.7 (339)			9
PhCH=CHCONMe ₂	+ Eu (fod) ₃	0.16	CDCl ₃		69.0 (336)			9
CH ₂ =CMeCONMe ₂			CDCl ₃		65.3 (290)			9
	+ Eu (fod) ₃	0.09	CDCl ₃		66.1 (314)			9
CONMe ₂	+ Eu (fod) ₃	0.10	CDCl ₃		69.5 (328)			9
PhCONMe ₂	+ Eu (fod) ₃	0.21	CDCl ₃		71.1 (346)			9

a. $\Delta G^\ddagger$ and $\Delta H^\ddagger$ are in kJ mol⁻¹; $\Delta S^\ddagger$ in J mol⁻¹ K⁻¹.

b. L = complexing agent; Lewis acid or LSR.

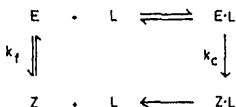
c. Ratio = molar ratio of L relative to substrate.

d. TCE = tetrachloroethane; FT = 3-fluorotoluene.

e. RB = rotating bond.

References: 1. Drakenberg *et al* (1972); 2. Stilbs (1973); 3. Stilbs (1971); 4. Martin *et al* (1980); 5. Hartman and Schrobilgen (1973); 6. Anet and Ghiaci (1979a); 7. Olofsson *et al* (1971); 8. Cheng and Gutowsky (1980); 9. Montaudo *et al* (1974).

the resulting stabilization of the E isomer. Evaluation of the rotational $\Delta G^\ddagger$ at various LSR concentrations, as given in table 31, revealed that while the barrier to the isomerization $Z \rightarrow E$ was not influenced appreciably, the barrier $E \rightarrow Z$ increased with increasing LSR concentrations. The process may be represented, after scheme I, as follows.



In other words, the contribution of k_c to the rotational rate is negligible for the $Z \rightarrow E$ process, but is increasingly more important for the $E \rightarrow Z$ process at higher concentrations of LSR.

Acknowledgement

The authors are deeply indebted to Dr R Reiter of Illinois State University for his linguistic assistance and continued encouragement.

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Affinities of organic compounds for solvent water; hydrophilic and hydrophobic character

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1. Introduction

Interactions between solutes in dilute aqueous solution generally require the stripping away of solvent water, at least in part, from the interacting groups. In addition to specific forces of attraction or repulsion that may be at work, apparent affinities between these groups can thus be considered to reflect the cost of removing each of them, at least in part, from solvent water. The potential magnitude of solvation effects on chemical reactions has become apparent with the development of new methods for determining rates and equilibria in the vapour phase. The presence of solvent water is found, for example, to alter the relative basicity of substituted amines by a factor of 10^{12} (Arnett *et al* 1972), and rates of attack by anions on alkyl halides are retarded in water by factors as large as 10^{18} (Olmstead and Brauman 1977). These reactions, involving changes in the localization of electrostatic charges, may exceed those that are likely to be encountered in reactions involving simple neutral molecules. Nevertheless it seems clear that, regardless of their nature, the affinity of organic compounds for solvent water exerts an important influence on their reactivity. Solvation effects also determine, at least in part, the strength and specificity of most biochemical "recognition" processes such as the binding of small molecules by enzymes, and the adoption of stable 3-dimensional structures by proteins and nucleic acids in water.

Because of remaining uncertainties about the structure of water, alone and in the neighbourhood of solutes, it is easier to appreciate the importance of solvation effects than to be sure of their physical origins. The empirical affinity of organic compounds and functional groups for watery surroundings has been a matter of continuing concern to experimentalists, who find it useful to refer to certain groups as being relatively hydrophilic or hydrophobic. It has been demonstrated that an attractive force exists, for example, at the interface between such dissimilar substances as liquid octane and liquid water (Harkins and Cheng 1921), and isolated methane and water molecules exhibit a modest affinity for each other in the vapour phase (Ungemach and Schaefer 1974). In this restricted sense, virtually all molecules are presumably attracted by water. Not all molecules, however, are attracted strongly enough to overcome the self-cohesive properties of water, as is necessary if they are to enter solution instead of merely adhering to the surface.

An experimental index of the affinity of a compound for solvent water (that is, for aqueous *surroundings*) is provided by its equilibrium constant for transfer from the dilute vapour phase (in which intermolecular interactions are negligible, and the solute exists in splendid isolation) to an aqueous solution so dilute that solute-solute

interactions can be neglected. Most chemically reactive substances exhibit a favourable equilibrium constant for transfer from vapour to water, attaining values as large as 10^8 for simple uncharged compounds bearing a single functional group (Wolfenden *et al.* 1981). Larger values are observed if several groups are present, and even the least strongly hydrated ions exhibit free energies of solvation of -30 kcal/mole or more. Hydrocarbons, on the other hand, show little affinity for watery surroundings. Acetylene, for example, exhibits an equilibrium constant of approximately unity for transfer from vapour to water, while paraffins actually favour the vapour phase (McAuliffe 1966).

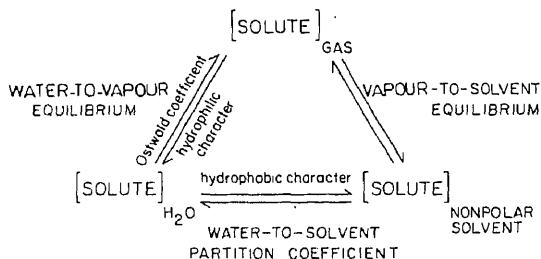
Of interest to many biologists is the equilibrium constant for transfer of a solute from dilute aqueous solution to dilute solution in an organic solvent. Such partition coefficients depend on the nature of the organic solvent that is used as a reference. Because biochemists are often concerned with permeability, or with the traffic of substances between water and biological membranes, the organic solvent is often chosen on the basis of its likely resemblance to the lipid interiors of membranes. Partition coefficients have proven to be extremely useful in correlating the chemical and biological behaviour of compounds in many systems (Hansch and Leo 1979).

Vapour-to-water equilibrium constants and water-to-solvent partition coefficients are related by the equilibrium constant for transfer of the solute from the vapour phase to dilute solution in the nonpolar solvent (figure 1). A natural expression of each of these distribution coefficients is in terms of the concentrations (mol/l) of solute in each phase, the distribution coefficient itself being dimensionless. For clarity, we will refer below to each of these equilibria simply by designating the phases between which transfer occurs. In the older literature, the equilibrium constant for transfer of a solute from water to vapour is defined as the "Ostwald coefficient". More recently, equilibrium constants for transfer from vapour to water have been taken as a measure of "intrinsic hydrophilic character" (Hine and Mookerjee 1975). Distribution coefficients describing the transfer of solutes from water to a nonpolar solvent have sometimes been regarded as an index of "hydrophobicity" (Nozaki and Tanford 1971) or "hydrophobic character" (Hansch and Leo 1979).

2. Water-to-vapour equilibria

2.1 Experimental determination

The intrinsic hydrophilic character of a molecule can be determined by evaluating the dimensionless equilibrium constant for its transfer from the dilute vapour phase to



Because it is difficult to analyze solutes at very low concentrations in the vapour phase, early measurements were confined to fairly volatile solutes that exhibit substantial vapour pressures over water. In order to extend these measurements to include polar molecules bearing functional groups of biological interest such as the peptide bond, it has proven necessary to resort to dynamic techniques similar to those first developed by Shaw and Butler (1930), and to use radioactivity as a means of detecting the solute in the vapour phase (Wolfenden 1976).

One kind of apparatus that can be used for such determinations is shown in figure 2. Each of the first three wash bottles contains radioactive solute at a known concentration in water, and is maintained at constant temperature. Water-pumped nitrogen is passed through these pots at a moderate rate (100 ml/min or less, for wash bottles of 150 ml capacity each), then through an empty wash bottle that serves as a spray trap, then through three wash bottles containing water alone, and finally through a wet-test flowmeter at equilibrium with the atmosphere. With such an arrangement, the pressure drop between the beginning and the end of the train is typically in the neighbourhood of 0.15 atmospheres. The concentration of radioactive material in the water traps is determined at intervals, and its chemical identity is established by radioautography of thin layer chromatograms or comparison of solvent-solvent distribution coefficients with those of authentic standards. Control experiments are used to test for effectiveness of the spray trap (radioactive acetate in alkaline solution is convenient for the purpose) and for efficient equilibration of carrier gas with solutions in the pots and traps. In a typical experiment involving radioactive acetamide, in which the number of pots and traps was varied, it was found that equilibration of the carrier gas with dissolved acetamide was over 90 % complete using a single pot; and that of the radioactivity transferred to the traps, over 90 % appeared in the first trap. It was demonstrated that appearance of radioactivity in the traps increased linearly with time, at a rate proportional to the rate of gas flow. To test for possible self-association of the solute in water, the rate of transfer was examined in, and shown to be unaffected by, the presence of nonradioactive solute at varying concentration in the pots (Wolfenden 1978).

In practical terms, this apparatus is useful for determining water-to-vapour

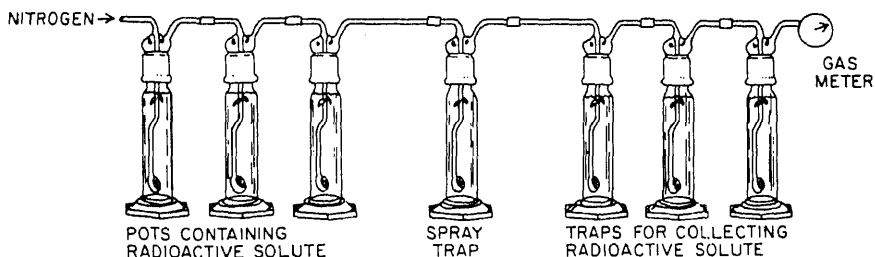


Figure 2. Apparatus for determining vapour pressures over water of relatively nonvolatile solutes (Wolfenden 1978; reprinted with permission from the American Chemical Society).

distribution coefficients falling in the range between roughly 10^{-5} and 10^{-10} . At this limit, compounds are not trapped efficiently in the collecting vessels, and below this range radioactivity becomes impractical as a means of detection, even using isotopes with short half-life such as ^{32}P .

For chromophoric substances, static measurements of distribution are conveniently performed using a spectrophotometric cuvette of 10 or 100 cm light path, made in such a way that the beam of the detecting instrument passes only through the vapour over a solution. The cuvette must be equipped with a thermostating jacket and any atmospheric condensation at the end-windows prevented by maintaining an appropriate temperature differential. Spectrophotometric measurements can be extended to low concentrations in the vapour phase (or to compounds with weak extinctions) by using multiple reflection cells that employ the ingenious "folded" design of White (1966). Such cells have been designed with light paths as long as 3 km. A practical advantage of spectrophotometric techniques in these studies is that, by detailed comparison of experimental spectra with spectra of the authentic pure material, it is sometimes possible to determine whether the solute in the vapour phase is associated with water molecules. A disadvantage is that it may be difficult to obtain an accurate extinction coefficient for the gaseous solute. If the solute's absorption spectrum in the vapour phase closely resembles the spectrum of the solute in a nonpolar solvent such as hexane, gross errors are unlikely to result from assuming that extinction coefficients are also similar.

When using these procedures, it is important to be sure that self-association of the solute does not occur in either of the phases that are being examined. Acetic acid, for example, exhibits a modest tendency to form dimers in the vapour phase, so that it is necessary to make a small correction in the observed vapour pressure in order to obtain the true vapour-to-water distribution coefficient of the monomer (Fredenhagen and Liebster 1932). Seldom encountered in experiments at reasonably high dilutions, self-association is normally detectable by a departure of the solute's vapour pressure from proportionality to its concentration in aqueous solution. Unrecognized self-association may lead to serious error if one attempts to estimate the distribution coefficient by simply combining the vapour pressure of the pure solute (in mol/l) by its solubility in water. In this way, results are obtained at only one concentration, corresponding to saturation, where self-association is most likely to occur.

2.2 Structural effects: monosubstituted hydrocarbons

Water-to-vapour distribution coefficients for some simple organic molecules of various chain lengths are displayed in figure 3. As noted in the early work of Butler and his colleagues (Butler 1937), the effect of increasing chain length is about the same for several homologous series, corresponding to an increment of about 26% for each methylene increment in the series of *n*-alkanes. In the six series for which five or more homologous compounds have been examined, the mean increment in distribution coefficient is $28.9 \pm 1.0\%$ (Wolfenden and Lewis 1976). There are no indications in these values or in distribution measurements involving the transfer of fat

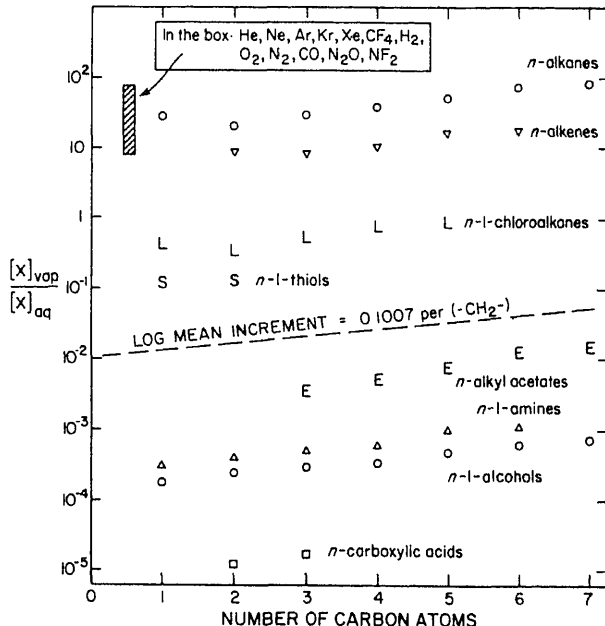


Figure 3. Water-to-vapour equilibria of normal aliphatic compounds, as a function of increasing chain length.

compounds for solvent water. Figure 4 shows some simple monosubstituted aliphatic compounds, arranged on a scale that spans 10 orders of magnitude.

In a general way, the hydrophilic character of these molecules appears to reflect the relative numbers of hydrogen bonds that they can form with solvent water. Methylguanidine, acetamide, acetic acid and ethyl acetate lie in the order expected on this basis. Not surprisingly, almost identical values are observed for acetaldehyde and acetone, but the lesser hydrophilic character of methyl acetate is somewhat unexpected.

In considering the hydrophilic character of N-methylacetamide, it is of interest to examine the effects of N-methylation, which might be expected to reduce the number of hydrogen bonds that this compound can form with solvent water. Instead, the hydrophilic character of N-methylacetamide slightly exceeds that of acetamide itself. A reduction in hydrophilic character occurs upon introduction of a second methyl group, in N,N-dimethylacetamide. It is surprising to note, however, that even N,N-dimethylacetamide is substantially more hydrophilic than acetamide itself. The strength of solvation of amides thus seems to be associated primarily with the carbonyl group, or with the dipolar character of the amide group taken as a whole. Amines exhibit somewhat similar behaviour. Methylamine and dimethylamine are similar to ammonia itself in hydrophilic character, while trimethylamine is somewhat less hydrophilic (table 1).

In both cases noted above, maximal hydrophilic character is observed in molecules that can form two kinds of hydrogen bonds with water, one as a hydrogen donor and one as a hydrogen acceptor (acetamide and N-methylacetamide in the amide series; ammonia, methylamine and dimethylamine in the amine series). Provided this

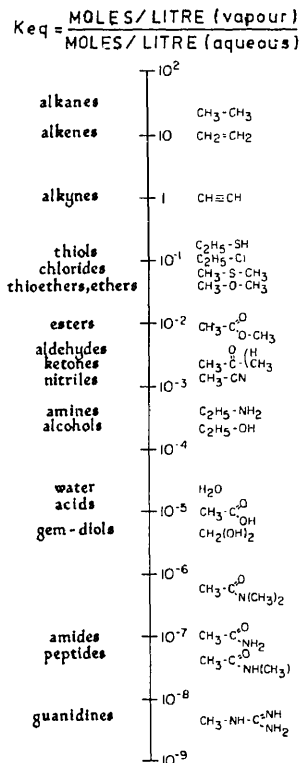


Figure 4. Water-to-vapour equilibria of uncharged organic compounds (redrawn, with additions, from Wolfenden 1978).

Table 1. Vapour/water distribution coefficients of amides and amines, 25° (Wolfenden 1978)

X	(X) _{vapour} /(X) _{water}
CH ₃ CONH ₂	7.6 × 10 ⁻⁸
CH ₃ CONHCH ₃	4.1 × 10 ⁻⁸
CH ₃ CON(CH ₃) ₂	5.4 × 10 ⁻⁷
NH ₃	7.7 × 10 ⁻⁴
CH ₃ NH ₂	2.9 × 10 ⁻⁴
(CH ₃) ₂ NH	7.2 × 10 ⁻⁴
(CH ₃) ₃ N	4.0 × 10 ⁻²

character, presumably because the additional hydrogen bonds that might have been influenced by these substitutions are in fact weak.

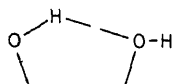
2.3 Interactions between polar groups

When two or more polar groups are present within the same molecule, their influence on its transfer from water to vapour is often found to be approximately additive, when expressed in terms of free energy or some other thermodynamic parameter. This relationship, first noticed by Butler and his associates (Butler 1937), has been amply

have been developed by Hine and Mookerjee (1975) and Cabani and Gianni (1979), and for partial molar heat capacities by Guthrie (1977). Departures from expectations based on additivity are of interest insofar as they may indicate the presence of special interactions between different parts of the solute molecule, or between regions of the solvent that surround different parts of the solute.

The more common kind of deviation is of a kind in which the affinity of a compound for watery surroundings is less than would have been expected from the sum of the effects of its substituents, as observed in monofunctional compounds. Glycerol and ethylene glycol exhibit equilibrium constants for transfer to the vapour phase that are, respectively, 7 and 3 orders of magnitude more favourable than had been expected from the behaviour of monohydric alcohols (Butler and Ramchandani 1935; Hine and Mookerjee 1975). Infrared spectra suggest that ethylene glycol is intramolecularly hydrogen bonded in the vapour phase, even at elevated temperatures (Buckley and Giguere 1967). Because of the apparent strength of this hydrogen bond, the affinity of this compound for watery surroundings is presumably less than it would otherwise have been.

It is difficult to be sure whether the strength of the intramolecular hydrogen bond, that appears to be formed by ethylene glycol in the vapour phase, is sufficient to account for its deviant behaviour. The length and nonlinearity of this hydrogen bond are remarkable, and it may be of interest to inquire whether methylene glycol, even more extreme in these respects, exhibits comparable behaviour. The water-to-vapour distribution coefficient of this covalent hydrate of formaldehyde can be estimated by combining the water-to-vapour distribution coefficients of anhydrous formaldehyde (obtained by extrapolation from a series of normal aliphatic aldehydes, Hine and Mookerjee 1975) and water, with the equilibrium constants for covalent hydration of formaldehyde in dilute aqueous solution (Lewis and Wolfenden 1973) and in the wet vapour phase (Hall and Piret 1949). The resulting estimated distribution coefficient for water-to-vapour transfer, 5.5×10^{-6} (shown on the scale of figure 4), is approximately 3.5 orders of magnitude larger than might have been expected from group contributions according to Hine and Mookerjee (1975), suggesting that similar factors may be at work in determining the unusual water-leaving tendencies of both ethylene glycol and methylene glycol. Either an intramolecular hydrogen bond can be formed in both cases in the vapour phase, or solvation of these molecules is ineffective for some other reason. These departures from expected behaviour are especially interesting in view of the resemblance of these diols to "tetrahedral" intermediates of the kind that are believed to be formed in displacement reactions of carboxylic acid derivatives in aqueous solution. If the strength of solvation of such intermediates is also less than that of starting materials, then such reactions may be retarded in water relative to the rates at which they would occur in the absence of water.



HO

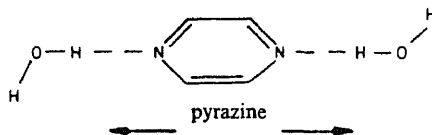
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HO

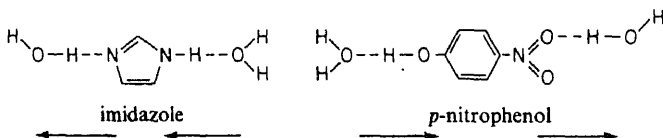
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Numerous other bifunctional compounds exhibit strong interactions that appear to reduce their affinities for dilute aqueous solution. Pyrazine, for example, is more than two orders of magnitude less hydrophilic than expected, presumably because hydrogen bonding of one nitrogen to water tends, by withdrawing electrons from the aromatic ring, to render the other nitrogen less basic than normal. In other compounds, distant polar interactions appear to result in a reinforcement of hydrophilic character. Imidazoles, for example, are extremely hydrophilic, whereas pyrroles and cyclopentadiene have low boiling points and limited solubility in water (Wolfenden *et al* 1981). The -NH- group of imidazole presumably interacts with water by acting as an acid in hydrogen bonding, the $=\text{N-}$ atom acting as a base in hydrogen bonding. These effects are expected to reinforce each other inductively, resulting in the interactions that are observed. Similarly the nitro and hydroxyl groups of *p*-nitrophenol appear to interact more strongly with water than do the nitro and hydroxyl groups of nitrobenzene and phenol, respectively: this appears readily understandable in terms of expected shifts of electron distribution through the ring (Hine and Mookerjee 1975).

Conflicting requirements of two hydrogen bonding substituents



Reinforcement of hydrogen bonding tendencies of two substituents



In general, when one hydrogen bond is formed, the resulting displacements of electron clouds and nuclei presumably tend to reduce the reactivities of neighbouring sites at which hydrogen bonds of the same kind might be formed, but to increase the reactivity of neighbouring sites where hydrogen bonds of the opposite kind might be formed. Comparing observations with ligands that are neutral or ionic, Huyskens (1977) has concluded that such interactions tend to arise from changes in hybridization and internuclear distances, rather than from electrostatic effects.

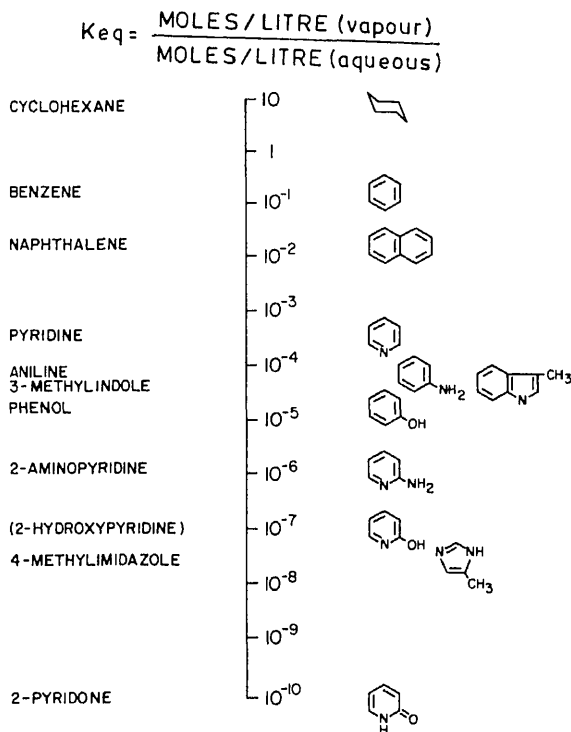


Figure 5. Water-to-vapour equilibria of cyclic compounds (data from Hine and Mookerjee 1975; Cullis and Wolfenden 1981).

perhaps because of their greater polarizability and the accessibility of their electron clouds to interactions with solvent water (figure 5).

The introduction of amino and hydroxyl substituents increases the hydrophilic character of benzene, although the effects are less striking than in aliphatic compounds (compare figures 4 and 5). Much larger increases are associated with the introduction of imino or keto substituents, as indicated by comparison of the hydrophilic character of various benzene and pyridine derivatives (Beak and Fry 1973; Cullis and Wolfenden 1981). As a result, heterocyclic bases undergo substantial changes in the positions of their amino-imino and keto-enol tautomeric equilibria when they are removed from water to a medium of low dielectric constant.

2.5 Directional character of solvation by water

Solvent shifts in the carbonyl stretching frequency of carboxylic acid derivatives, that occur upon transfer from the vapour phase to deuterium oxide, are roughly related to their relative hydrophilic character; in addition, the effects of methyl substitution on water-to-vapour transfer of amides suggest that hydrogen bonds involving the carbonyl oxygen are of substantially greater importance than those involving the N-H

bonds. Recent x-ray diffraction studies on the protein rubredoxin seem to bear out this prediction, as reflected by the positions of water oxygen atoms that are sufficiently immobile to appear in the electron density map of the 51 water molecules located within hydrogen bonding distance of peptide bonds in this protein containing 53 amino acids, 38 are associated with carbonyl oxygen and 13 are associated with peptide N-H groups (Watenpaugh *et al* 1978). Trypsin (Bode and Schwager 1975) and actinidin (Baker 1980) exhibit a similar bias in favour of carbonyl hydration.

Other evidence suggests that regions of solvent water, surrounding different parts of some solutes, interact in a way that departs from expectations based on simple additivity relationships. In a series of normal carboxylic acids, decreases in volume that accompany ionization at atmospheric pressure show a surprisingly large *range* of values that would be difficult to explain without supposing that hydrocarbon substituents influence the structure of water in the vicinity of the ionizing groups (Kauzmann *et al* 1962). In a series of aliphatic aldehydes, decreases in molar volume that accompany covalent hydration range from -4 ml for formaldehyde to a limiting value of about -13 ml for isobutyraldehyde. Effects of substituents on volume of hydration are comparable with those observed for the volume of ionization of carboxylic acids. These substituents are not expected to influence reaction volumes markedly through direct steric or inductive effects, so that their influence is probably exerted through the solvent (Lewis and Wolfenden 1973).

Efforts to calculate the relative affinities of water for different sites on solutes, using molecular orbital methods, are currently widespread (for a review, see Pullman and Pullman 1975). In one recent study, probability densities have been generated for solvent water molecules in immediate contact with various regions of trans-glyoxal. As expected, specific solvation sites tend to be found in regions toward which the lone pairs of electrons of the solute oxygen atoms are directed (Mehrotra *et al* 1981). When these theoretical approaches become sufficiently refined to allow predictions that can be verified experimentally, major advances in our understanding of the details of solvation may become possible.

3. Water-to-solvent partition coefficients

Partition coefficients between water and a second solvent can be considered to resemble water-to-vapour equilibria, if the vapour phase is regarded as a 'second solvent' that neither attracts nor repels solutes. Depending on the nature of the solute and the second solvent, varying degrees of attraction may be encountered, so that solute-solvent pair presents a complex problem in structural analysis. Despite this complexity, water-to-solvent partition coefficients are of considerable interest and practical importance in chemistry and biology.

3.1 *Experimental determination*

The literature concerning water-to-solvent distribution coefficients is very extensive. However not all the observed results were obtained at sufficient dilution to ensure that self-association of solute did not occur. There is also the often-unrecognized possibility, sometimes encountered in water-to-vapour distributions, that water may have entered

the problem can be avoided entirely by measuring the solubility of the solute in each of the pure solvents, and calculating a distribution coefficient from the ratio of solubilities. This latter procedure also allows the determination of imaginary partition coefficients that could never be measured in practice, involving distributions between solvents that are miscible. Its disadvantage is that it does not permit variation of the concentration of solute in each phase under otherwise constant conditions, so that it is difficult or impossible to determine whether self-association has occurred.

A practical problem that is sometimes encountered in determining distribution coefficients, by shaking together two immiscible solvents, is the formation of emulsions that may or may not be visible. The use of centrifuge of fairly large capacity solves this problem. When a distribution is extremely one-sided, it is sometimes necessary to determine the concentration in the dilute phase by using a very large volume of it, and then back-extracting with a small volume of the favoured solvent. The distribution coefficient can then be calculated by difference. To avoid errors due to absorption on glass surfaces, it is preferable that both phases be analyzed directly, and this is usually possible if radioactive solutes are employed.

Leo *et al* (1971) have discussed these potential difficulties in detail, and have recommended that the term 'partition coefficient' be used only to describe data that have been corrected for dimerization, ionization, etc., and refer to the distribution of a single species between two phases.

3.2 *Structural effects*

Partition coefficients between water and a second solvent can be considered to resemble water-to-vapour equilibria, if the vapour phase is regarded as an ideal 'second solvent' that neither attracts nor repels solutes. No real second solvent approaches this ideal. Condensed phases are not only self-associated but also attract solutes by weak forces with a greater or lesser degree of specificity. Fluorocarbons approach the ideal of noninteracting solvents much more closely than do hydrocarbons (Reed 1964; Hamza *et al* 1981), but for reasons of cost and practical applicability, the great majority of water-to-solvent equilibria have been measured with liquid hydrocarbons serving as the second phase. Each solute-solvent pair thus represents a unique problem in structural analysis, more complex than the analysis of equilibria between water and the vapour phase. In practice, the nonaqueous solvent (hexane, for example) is sometimes chosen for its nonpolarity, and partition coefficients are then expected to reflect hydrogen-bonded interactions with water in the same sense as do water-to-vapour distribution coefficients. Alternatively, the nonaqueous solvent (1-*n*-octanol, for example) is sometimes chosen for a mixed set of properties, being capable of hydrogen-bonding interactions with the solute yet retaining considerable nonpolar character.

A number of common nonaqueous solvents have been arranged by Leo according to their 'lipophilicity', that is their water content at saturation. This scale can be used to correlate the thousands of distribution coefficients that have accumulated in the literature, involving more than 20 different solvent systems. Progress in refining these correlations has been reviewed recently (Recker 1977; Hansch and Leo 1979). The partition coefficient is assumed to receive contributions that are additive in terms of free energy, from the various groups of which the molecule is composed. It is of interest to compare the resulting fragment constants for various organic groups, expressing their

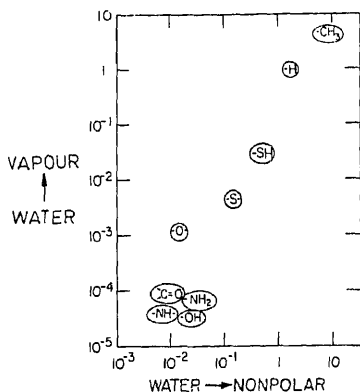


Figure 6. Substituent constants for transfer from water to vapour (from Hine and Mookerjee 1975) plotted as a function of fragment constants for transfer of organic substituents from water to nonpolar solvents (from Hansch and Leo 1979).

derived from water-to-vapour equilibria of organic solutes (figure 6). Considering that the data bases are different, the correspondence between the two sets of constants is not bad. The slope of the line that would relate the entries in figure 6 is somewhat greater than unity, consistent with the possibility that increasing polarity tends to draw substituents from the vapour phase into organic solvents (as might be expected due to the operation of dipole-induced dipole interactions).

4. Transfer of hydrocarbons from water to nonpolar solvents: Sources of 'apolar bonding' or the 'hydrophobic effect'

Saturated hydrocarbons tend to leave water and enter other solvents. One can ask whether solute molecules tend to leave water and enter less polar solvents mainly 'because they are repelled by water'; or whether they do so 'because they are attracted to the less polar solvent'. This question may be analyzed, if one chooses, by referring to some absolute standard of reference such as the vapour phase, that neither attracts nor repels solutes. Framing the question in these terms, it is found that methane exhibits an appreciable water-leaving tendency, with an equilibrium distribution between water and the vapour phase of 27 in favour of the vapour phase. This tendency increases in the normal alkanes as follows: methane 27, ethane 20, propane 29, butane 38, pentane 51, hexane 74, heptane 83. For each methylene increment ($-\text{CH}_2-$, that is), transfer to the vapour phase is enhanced by an average factor of 1.26, equivalent to 0.136 kcal in free energy. This increment is about the same in the normal series of hydrocarbons, acetic

In summary:

- (i) saturated hydrocarbon molecules have an appreciable tendency to leave water, and are thus 'hydrophobic' in any sense of the word.
- (ii) this tendency is only slightly enhanced by the increasing size of the hydrocarbon solute.
- (iii) increasing size of the hydrocarbon (addition of a 'methylene increment') strongly enhances the tendency to leave water and enter a nonpolar solvent such as a hydrocarbon.
- (iv) most of the effect described in (iii) is matched by an increasing tendency to leave the vapour phase and enter a hydrocarbon solvent (figure 7).

The effect of a methylene increment, on the free energy associated with simple removal of a solute from water, is small at room temperature, but there are substantial changes in other thermodynamic parameters. Removal of nonpolar molecules or groups from water is accompanied by increases in entropy (and volume) and by a compensating uptake of heat from the surroundings. Thus 'apolar' or 'hydrophobic' bonds (*i.e.* the biologically important association of nonpolar groups in aqueous surroundings) are distinguished by a tendency to become stronger with increasing temperature (Kauzmann 1959; Némethy and Scheraga 1962). Because the properties of liquid water, and of water of solvation in particular, are still dimly understood, there has been continuing discussion of the likely origins of the entropy increases that accompany the formation of hydrophobic bonds, on the removal of hydrocarbons from water to the vapour phase.

The self-cohesive properties of water, although not unique (Evans *et al* 1981), are unusual (Edsall and Wyman 1958). It seems reasonable to suppose that changes in the properties of water in the immediate neighbourhood of the solute could account for the loss of entropy that accompanied introduction of a nonpolar molecule or methylene increment into water from the vapour phase or from a nonpolar solvent. Frank and Evans (1945) suggested that this might imply the formation around solutes of a kind of clathrate or iceberg structure, in which water molecules were more ordered than in the bulk solute, but did not resemble Ice I in any literal sense. Recent evidence suggests that entropic effects associated with introducing nonpolar solutes into water may arise, not so much from restrictions on the mobility of water molecules, as from restrictions on the mobility of solutes when they are introduced into the aqueous environment (Aronow and Witten 1960). Solutes experience a 3- to 5-fold enhancement in ^{13}C spin-lattice relaxation times when they are transferred to water from nonhydroxylic solvents of similar viscosity, so that water appears to be unusual in the restrictions that it imposes on the motion of dissolved solutes (Howarth 1975). In normal aliphatic compounds of increasing size, solubility might (according to this view) be reduced by

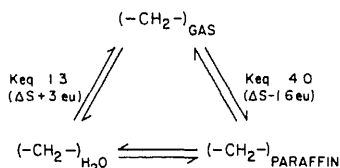


Figure 7. Equilibrium constants and entropies associated with transfer of methylene increments between water, nonpolar solvents and the vapour

steroids and cycloalkanes display considerably lower activity coefficients in water than nonrigid compounds, with reference both to nonpolar solvents and the vapour phase (Osinga 1979). Such disparate solutes as methane, ammonia and water, show almost the same entropy of solution, despite very great differences in their affinities for solvent water and the restrictions that polar interactions might have been expected to impose on the solvent. For a large group of rare gases, alcohols, amines, and aromatic hydrocarbons, entropies of solution can be predicted with remarkable accuracy by assuming that the gaseous compound loses a constant fraction (46%) of its entropy when it is brought into dilute solution in water (Wertz 1980). These findings suggest that bringing a molecule from the vapour phase into aqueous solution is something like confining it in a box, with the walls of which its entropy gives no evidence of specific interaction. Instead, specific polar interactions are evidently manifested almost entirely in the enthalpy term.

5. Water affinities and biochemistry

Most metabolic transformations in biochemistry occur in a watery environment, their overall free energies determined in part by the relative free energies of solvation of reactants and products. Solvation effects are believed to make very important contributions to the free energies of hydrolysis of anhydrides of phosphoric acid, such as ATP (George *et al* 1970; Hayes *et al* 1975). It has been shown that the large negative free energy of aminolysis of esters, a critical step in protein biosynthesis, is more than completely matched by the stronger hydration of products than reactants, being endergonic in the vapour phase (Wolfenden 1976). Similar considerations apply to the hydrolytic deamination of adenosine (Cullis and Wolfenden 1981).

Catalysis by enzymes, on the other hand, involves partial reactions that occur in the relatively waterless environment of the active site. In order that catalytic rate enhancement be observed, the theory of absolute reaction rates suggests that the altered substrate must be bound more tightly in the transition state than in the ground state (Pauling 1946; Jencks 1966; Wolfenden 1969). It appears inevitable that binding must involve the stripping away, at least in part, of solvent water from the species that is bound, and that differences between binding affinities of the altered substrate in the ground state and in the transition state (or stable analogs of these species) may reflect differences between their free energies of solvation (Wolfenden 1972). A probable case in point has been uncovered by the work of Lienhard and his associates (Crosby and Lienhard 1970; Gutowski and Lienhard 1976) on pyruvate dehydrogenase; the catalyzed reaction probably proceeds through intermediates that are very much less polar than the reactants, and is strongly inhibited by analogs of comparable structure. There are also several cases of the opposite kind, in which transition state analogs are bound in their most fully ionized forms, suggesting the intervention of highly charged intermediates which are held by the active site of the enzyme just as a metal ion is held by an ionophore or chelating agent (Wolfenden 1980).

The polar character of amino acids serves as a critical determinant of their tendencies to be found at the surface of globular proteins (Kauzmann 1959; Perutz 1965), and these tendencies prove to be closely correlated with the absolute affinities of amino acid

side-chains for solvent water. Equilibrium constants for transfer of the common amino acid side-chains from water to the vapour phase are displayed in figure 8, and figure 9 shows the relationship between these values and the tendencies of the corresponding amino acids to be found at the surface of globular proteins, in contact with the solvent (Wolfenden *et al* 1981).

The extreme position in these relationships of arginine, the 'Pluto' of amino acids, is of special interest. Comparisons of the physical properties of several proteins has shown that quaternization of primary amino groups results in increased stability to thermal denaturation (Tuengler and Pfeleiderer 1977) and tritium exchange (Cupo *et al* 1980), and the arginine/lysine ratio seems to be positively correlated with thermal stability in redox proteins from several organisms (Argos *et al* 1979). These findings seem understandable in terms of the marked reluctance of arginine residues to be withdrawn from water, as might be necessary during the course of protein denaturation.

In nucleic acids, base pairing and stacking interactions occur in competition with solvent interactions of the participating groups (Ts'o 1979). Keto-enol and amino-

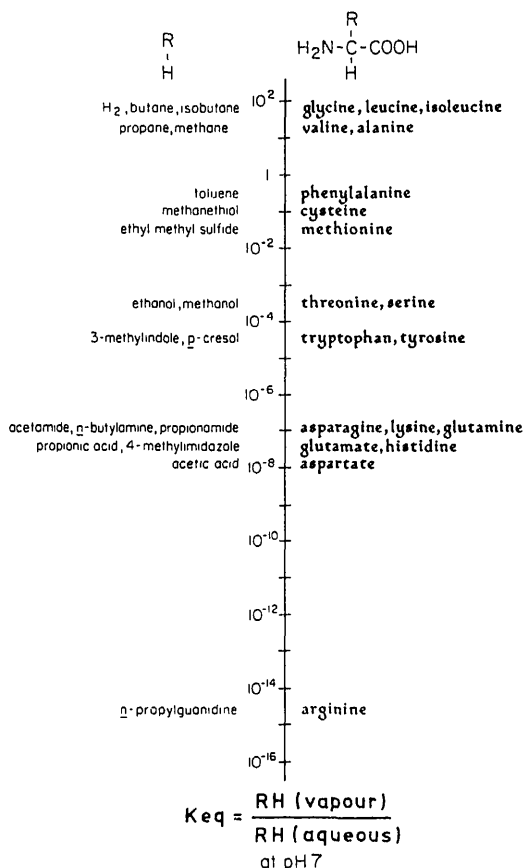


Figure 8. Equilibrium constants for transfer of side-chain of the common amino acids from

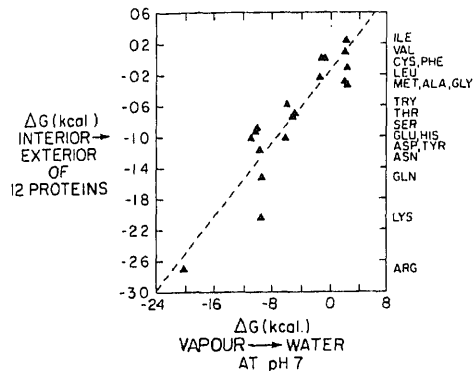


Figure 9. Free energies of transfer of amino acid side-chains from the interior to the exterior of protein molecules, plotted as a function of their free energies of transfer from water at pH 7, to the vapour phase (Wolfenden *et al* 1981; reprinted with permission from the American Chemical Society).

imino tautomeric equilibria are dependent on the relative hydration of the tautomers, which might be expected to differ considerably from each other; as shown in figure 5, for example, 2-pyridone is some 4 orders of magnitude more strongly hydrated than its tautomer, 2-hydroxypyridine (Beak and Fry 1973; Cullis and Wolfenden 1981). In neutral aqueous solution, equilibria of nucleic acid bases have been found to favour keto over enol tautomers, and amino over imino tautomers, by factors in the neighbourhood of 10^4 – 10^5 . During biosynthesis of nucleic acids and proteins, errors in base pairing due to the occurrence of rare tautomers may lead to mutational events (Watson and Crick 1953; Topal and Fresco 1976). Errors that would depend on the occurrence of rare enol tautomers thus appear more likely to occur in nonpolar environments (such as the active sites of certain enzymes) than in water itself.

'Apolar' or 'hydrophobic' bonding has aroused considerable interest because of its relationship to protein folding and the properties of biological membranes. The extensive literature concerning these phenomena, and their interpretation at the molecular level, is beyond the scope of the present article. The interested reader is referred to an excellent discussion by Klapper (1973), placing apolar bonding in the context of the scaled particle theory of Pierotti; and to recent reviews by Richards (1977) and by Némethy *et al* (1981) in which the problem of protein folding is considered in detail.

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Molecular interactions and dynamics in liquid crystals

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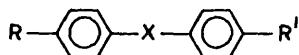
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1. Introduction

The anisotropy of molecular shape is a fundamental requirement for the formation of liquid crystals. Until recently, the rule was that the molecule has to be long and rod-like for mesomorphism to occur, but it has now been established that simple disc-shaped molecules may also form stable mesophases (Chandrasekhar *et al* 1977). Liquid crystallinity may be induced by purely thermal effects (thermotropic mesomorphism) or by the influence of solvents (lyotropic mesomorphism). We shall be concerned here only with the former type of mesomorphism, that too in relatively low molecular weight compounds, and not deal with lyotropics or high molecular weight systems like mesomorphic polymers.

Thermotropic liquid crystals exhibit a rich variety of phases, the broad structural features of which are summarised in table 1. A description of the physical properties of these phases may be found in standard books and articles on the subject (see, for example, Chandrasekhar 1977, 1983; de Gennes 1974). It should be pointed out, however, that the detailed structures are not known with certainty for a number of these phases, and some confusion remains in regard to the structural classification of the more ordered smectic modifications (Gray 1981; Demus *et al* 1980). Recent high resolution x-ray studies have shown that several of these modifications possess three-dimensional positional order, though the interlayer forces are extremely weak, very much weaker than in the ordinary crystalline solid. These highly ordered phases cannot therefore be called liquid crystals in the strict definition of the term. As far as the newly discovered phases of disc-like molecules are concerned, the subject is still very much in its infancy. For these reasons, the discussion in this article will be confined largely to those liquid crystalline phases whose structures are known unambiguously and which have been investigated in detail both experimentally and theoretically from the standpoint of molecular interactions and dynamics, though of course references will be made to the other phases wherever it is relevant.

Typically, the simplest rod-like mesogenic molecules have a structure of the form



where both R and R' may be hydrocarbon chains, or R a small group like CN, NO₂, Br, etc., and R' a chain; the middle portion of the molecule is a more or less rigid aromatic core with a central linkage group X, though in some molecules X may be absent altogether. Also, in some cases one or both the phenyl rings may be saturated. Examples

Table 1. Structural classification of thermotropic liquid crystals.

<i>Rod-like molecules</i>	
Nematic (N)	Long range orientational order but no long range translational order (figure 1a)
Cholesteric (Ch)	Chiral nematic (figure 1b)
Smectic A (S_A)	Liquid-like layers with upright molecules (figure 1c)
B (S_B)	Two distinct types of S_B have been identified: (i) 3D crystal, hexagonal lattice, upright molecules (Moncton and Pindak 1979), (ii) stack of interacting 'hexatic' layers with in-plane short range positional correlation and long range 3D six-fold 'bond-orientational' order (Pindak <i>et al</i> 1981)
C (S_C)	Tilted form of S_A (figure 1d)
C^* (S_{C^*})	Chiral S_C with twist axis normal to the layers (see figure 7)
D (S_D)	Cubic
E (S_E)	3D crystal, orthorhombic, upright molecules (Doucet <i>et al</i> 1975)
F (S_F)	Monoclinic ($a > b$) with in-plane short range positional correlation and weak or no inter-layer positional correlation (Gray 1981; Leadbetter <i>et al</i> 1980; Gane <i>et al</i> 1981) (tilted hexatic?)
G (S_G)	3D crystal, monoclinic ($a > b$) (Gray 1981; Gane <i>et al</i> 1981)
G' ($S_{G'}$)	3D crystal, monoclinic ($b > a$) (Gane <i>et al</i> 1981)
H (S_H)	3D crystal, monoclinic ($a > b$) (Leadbetter <i>et al</i> 1980; Gane <i>et al</i> 1981)
H^* (S_{H^*})	Chiral S_H with twist axis normal to the layers
H' ($S_{H'}$)	3D crystal, monoclinic ($b > a$) (Gane <i>et al</i> 1981)
I (S_I)	monoclinic ($b > a$), possibly hexatic with slightly greater in-plane positional correlation than S_F (Gane <i>et al</i> 1981; Pindak <i>et al</i> 1982)
I^* (S_{I^*})	Chiral S_I (Pindak <i>et al</i> 1982)
<i>Disc-like molecules</i> (Chandrasekhar 1982; Destrade <i>et al</i> 1981a)	
D_{hd}	Columnar structure (D) with a hexagonal packing of the columns and a disordered or liquid-like arrangement of the discs in each column (figure 2a, b)
D_{ho}	hexagonal but with an ordered arrangement of the molecular cores in each column
D_{rd}	rectangular, disordered (figure 2c)
D_t	tilted columnar structure (figure 2d)
N_D	nematic-like arrangement of discs (figure 2e)
N_D^*	Chiral N_D

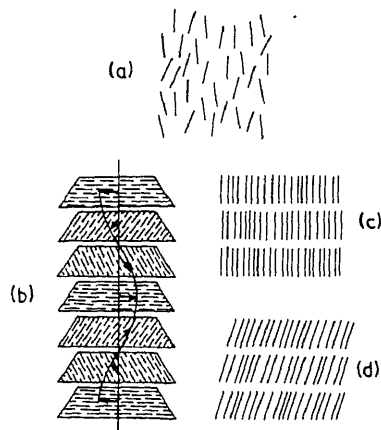


Figure 1. Liquid crystals of rod-like molecules: (a) nematic, (b) cholesteric, (c) and (d) normal and tilted smectic structures.

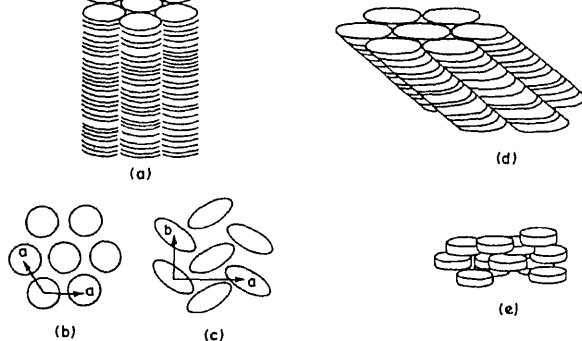


Figure 2. Liquid crystals of disc-like molecules: (a) columnar phase with upright columns; (b) and (c) hexagonal and rectangular modifications of the upright columnar structure; (d) tilted columnar phase; (e) 'nematic' phase.

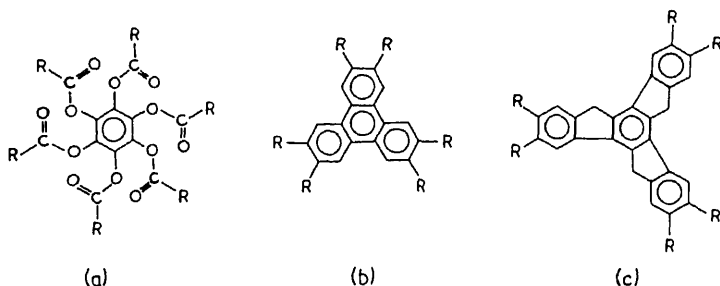


Figure 3. Disc-shaped mesogens: (a) hexa-substituted esters of benzene (Chandrasekhar *et al* 1977); (b) hexa-substituted esters or ethers of triphenylene (Billard *et al* 1978; Destrade *et al* 1979); hexa-*n*-alkyl or alkoxybenzoates of triphenylene (Destrade *et al* 1980); (c) hexa-*n*-alkanoates of truxene (Destrade *et al* 1981b).

p-quinquephenyl, a string of five benzene rings in a row without any end chains. To date, several thousands of mesogens are known (see, for example, Demus *et al* 1974; Demus and Zashke 1984; Kelker and Hatz 1980) and most of them have rather more complex structures than indicated above. The effect of the central linkage group, the terminal and lateral substituents, and the role of the end chains in determining mesomorphic properties have been extensively discussed (Gray 1976, 1979) and therefore will not be repeated here. The stability of the mesophase is a delicate balance of dispersion forces and steric effects, and, if the molecule is polar, the permanent dipolar forces as well. It is clear that for molecules of such complexity these interactions are by no means easy to calculate.

Comparatively few disc-shaped mesogens have been synthesised so far (Chandrasekhar 1982). Three typical molecular structures are shown in figure 3.

2. Molecular interactions

2.1 Nematic liquid crystals

The nematic is the simplest type of liquid crystal and the problem of the molecular interactions responsible for its stability has been the subject of numerous discussions.

The first successful 'mean field' theory of this phase was developed by Maier and Saupe (1958–60), who used a single particle potential of the form

$$U_i = -AsP_2(\cos\theta_i) \quad (1)$$

where A depends on the molecular species and is a function of the density ρ , $s = \langle P_2(\cos\theta) \rangle$ is the orientational order parameter, and $P_2(\cos\theta)$ the Legendre polynomial of the second order. Such a potential is consistent with the fact that the director (or the vector $\mathbf{n}$ defining the axis of preferred orientation of molecules) is *apolar*. Maier and Saupe assumed that this potential arises from the dipole-dipole part of the anisotropic dispersion forces and thus put $A \propto \rho^2$. However, experiments on the pressure dependence of the order parameter indicate that $A \propto \rho^\gamma$, where $\gamma = 4$ for PAA (*p*-azoxyanisole, McColl and Shih 1972) and in some other cases even greater than 4 (Horn 1978; Horn and Faber 1979). On the other hand, an argument due to Cotter (1977a) shows that thermodynamic consistency of the mean field theory requires that $\gamma = 1$. But, regardless of the magnitude of γ , the theory leads to a universal value of $s \approx 0.43$ at T_{NI} , the nematic-isotropic (NI) transition point, for all substances. Experimentally, there are small but systematic deviations from this universal value which can be accounted for by including higher order terms in the potential function (Chandrasekhar and Madhusudana 1971; Humphries *et al* 1972). The principal drawback of the mean field approximation is that it predicts a heat of transition which is much too high, usually by a factor of 2 or 3. The theory can be improved significantly by taking into account near neighbour orientational correlations in terms of a Bethe cluster (Madhusudana and Chandrasekhar 1973a; Madhusudana *et al* 1977; see also Ch. 2 of Chandrasekhar 1977), but quantitatively the agreement is still not too satisfactory.

Another microscopic approach is to treat the system as an assembly of hard rods. The first theory of the phase transition in a hard rod system was developed by Onsager (1949). The properties of such an 'athermal' system depends entirely on the density, and the basic problem is to evaluate φ_N , the excess free energy relative to an ideal gas, with a suitable orientational distribution function of the rods. Onsager made a virial expansion of φ_N and retained only the second virial coefficient. This approximation is valid for low densities and thus for very long rods with a length to breadth ratio ≈ 100 . Zwanzig (1963) could evaluate higher virial coefficients by restricting the molecules to take up only three mutually perpendicular orientations. Flory (1956) and Flory and Ronca (1979) used a lattice model and were able to make calculations at relatively high densities. However, these descriptions are useful only for long polymeric molecules (Straley 1973), the predicted s at T_{NI} being ≈ 0.85 .

For relatively short rods (of length to breadth ratio ≈ 3 –5) and high densities, the scaled particle theory provides a convenient method of evaluating φ_N . Cotter (1974, 1979) has developed the most complete form of the theory as applied to nematic liquid crystals. In this scheme, the reversible work $w_i(\alpha, \lambda, \rho)$ of adding a scaled rod (α, λ being the scaling parameters along the length and breadth of the molecule)

PAA. Recently, another method has been used (Savithramma and Madhusudana 1980; Madhusudana 1981) for evaluating φ_N by extending the Andrews (1975) model for calculating the equation of state of a liquid. Basically, this model depends on the recognition that the reciprocal of the thermodynamic 'activity' is merely the probability of being able to insert a particle into the given system such that the extra particle does not overlap with other particles. The model leads to a better description of the nematic phase than that given by the scaled particle theory. Computer simulation studies have also been carried out for hard spherocylinders but till now only for the isotropic phase (Vieillard-Baron 1974; Rebertus and Sando 1977; Nezbeda and Boublik 1978).

It is clear that a realistic theory of nematics should incorporate the attractive potential between the molecules *as well as* their hard rod features. Several hybrid models have been proposed on the basis of the lattice theories (Alben 1971). More recently, equations of state have been derived based on the Percus-Yevick and BBGKY approximations for spherical molecules which are subject to an attractive Maier-Saupe potential (Ypma and Vergoten 1977; Wagner 1981). However, these models lead to $\gamma \approx 1$, where $\gamma = [\ln T / \ln V]_s$, is a measure of the relative importance of volume compared to that of temperature in determining the variation of s near T_{NI} . (In the mean field models which make use of only an attractive potential γ is equal to the exponent of ρ .) The anisotropic shape of the molecule has to be explicitly considered to obtain higher values of γ .

Cotter (1977b; for an up-to-date review, see Cotter 1983) has extended the scaled particle theory to include an attractive potential of the type

$$U_i = -v_0\rho - v_2\rho s P_2(\cos\theta_i).$$

The resulting distribution function is similar to that in the Maier-Saupe theory, except that the coefficient of the potential has the form $[(v_2\rho/kT) + \Lambda(\rho)]$, i.e., a temperature-dependent attractive part and an 'athermal' part corresponding to the hard particle contribution. The theoretical results can be improved further by using the Andrews model (Savithramma and Madhusudana 1980; Madhusudana 1981). These last two approaches yield promising results—for example, it turns out that $\gamma \approx 4$ for PAA without violating Cotter's thermodynamic consistency condition that the mean field potential should be $\propto \rho$. Certain generalised van der Waals models (Gelbart and Baron 1977; Cotter 1977c) have also been proposed but these lead to results which are essentially similar to the scaled particle theory with a superposed attractive potential. Luckhurst and Romano (1980) have carried out a Monte-Carlo computer simulation study on 256 cylindrically symmetric rigid particles with an attractive potential. They have made calculations for a certain value of an 'anisotropy parameter' and found a weak NI transition, and compared the results with the predictions of the Maier-Saupe theory.

In all these models, the molecules have been taken to be cylindrically symmetric, but most real nematogens have lower symmetry which lowers the order parameter at T_{NI} . Recent calculations (Alben 1973; Straley 1974; Luckhurst *et al* 1975; Gelbart and Barbooy 1979) have shown the importance of taking this into consideration. Moreover, the assumption that the molecule is a rigid rod is an oversimplification. Attempts have been made (Marcelja 1974; Martire 1974; Dowell and Martire 1978; Luckhurst 1984) to calculate the contribution of the flexible end chain to the ordering process, and to

permanent dipolar interactions cannot be neglected, but these give rise to certain special effects which we shall discuss later in greater detail (§3).

Until fairly recently, only $\langle P_2 \rangle$ was accessible experimentally, but now a method is available for measuring both $\langle P_2 \rangle$ and $\langle P_4 \rangle$. The technique, developed by Jen *et al* (1973) involves polarized Raman scattering measurements using aligned samples. A few cyano-compounds have been investigated by this method making use of the $C\equiv N$ stretching vibration for the Raman measurements. It has been found in most cases studied so far that $\langle P_4 \rangle$ is negative for at least a part of the nematic range (Jen *et al* 1973; Miyano 1978; Prasad and Venugopalan 1980, 1981; Dalmolen *et al* 1984). Using the observed values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ one can calculate a truncated angular distribution function (Jen *et al* 1973). The results indicate that the molecule has a strong tendency to be tipped away from the nematic axis, which cannot be explained by any of the theories discussed above. More data are needed to confirm these findings, but in any case it would appear that this is an important unsolved problem (Luckhurst and Vitoria 1982; Feng *et al* 1983; de Jeu 1983).

2.2 Cholesteric liquid crystals

The cholesteric is also a nematic type of liquid crystal except that the director does not have a uniform orientation in space but is twisted in the form of a helix (figure 1b). Such a structure is obtained when the molecules are chiral, or even when a small amount of an optically active compound is added to a nematic. The energy needed to twist the director is very small compared to the nematic potential. However, to explain the helical structure the chiral nature of the molecules has to be explicitly taken into account. There have been a few attempts to derive a molecular theory of the cholesteric phase. Schröder (1979) has discussed the general potential between chiral molecules based on their symmetry. Goossens (1971) has shown that the dipole-quadrupole part of the dispersion forces is the lowest order contribution to the chiral interaction leading to the helical arrangement of the director. Van der Meer and Vertogen (1979a) have developed a Maier-Saupe type mean field theory by including in the potential a term of the type $-K(\mathbf{a}_i \cdot \mathbf{a}_j)(\mathbf{a}_i \times \mathbf{a}_j \cdot \mathbf{u}_{ij})$, where $\mathbf{a}_i$, $\mathbf{a}_j$ and $\mathbf{u}_{ij}$ are unit vectors along the long axes of the molecules i, j and along the line connecting the two molecules respectively. They have argued that this form of the potential can be obtained by assuming that the molecule can be modelled to have a number of linear polarisabilities which are regularly situated on a twisted cylindrical surface. Contributions to the above form of the potential can also come from the chiral shape of the molecules (for example, a twisted cog-wheel). The two contributions need not have the same sense and may account for the helix inversion found in some nematic-cholesteric mixtures as a function of concentration. They have also shown that a part of the temperature variation of the pitch is connected with the variation of $(k_{11} - k_{33})/k_{22}$, where k_{11} , k_{22} and k_{33} are the splay, twist and bend elastic constants of the material.

2.3 Smectic and columnar liquid crystals

Quantitatively speaking, much less is understood about molecular interactions in the smectic phases, and only S_A and S_C have been discussed in any detail.

McMillan (1971, 1972) extended the Maier-Saupe theory of nematics to the S_A phase by assuming an ordering potential between the directors in the plane of the smectic

particle is then given by

$$V_i = -V_0 P_2(\cos \theta_i) [s + \alpha \sigma \cos(2\pi z/d)]$$

where d is the layer spacing, $\sigma = \langle P_2(\cos \theta) \cos(2\pi z/d) \rangle$ is an order parameter coupling the translational and orientational ordering, and $\alpha \equiv 2 \exp[-(r_0/d)^2]$ is a molecular parameter where r_0 is the dimension of the rigid core of the molecules. The theory predicts that for $\alpha > 0.98$, the S_A transforms directly to the isotropic phase, while for $\alpha < 0.98$ there is an AN transition followed by an NI transition at a higher temperature. For $\alpha \leq 0.7$ the AN transition is of second order. α increases with the length of the end chain of the molecule. The general conclusions of the theory are in accord with the observed trends. To allow for the fact that real molecules are not cylindrically symmetric but lath-like, the theory has been extended recently to include the possibility of a biaxial S_A phase (Matsushita 1981).

Physically, the strongest attractions between two smectogenic molecules are between their aromatic cores and hence as the end chain length is increased, the cores would prefer to arrange themselves in layers, thus leading to the formation of the smectic phase. However, it must be pointed out that there are some notable exceptions to this rule; for example, *p*-sexiphenyl which has no end chain has been reported to exhibit the S_A phase (Lewis and Kovac 1979).

Generally speaking, the presence of polar groups in the molecule appears to favour the formation of smectic phases. In particular, lateral dipole moments are essential for the occurrence of the S_C phase. Van der Meer and Vertogen (1979b) have shown that the forces between lateral dipoles and the 'induced' dipoles at the centres of neighbouring molecules can lead to a tilted structure as in the S_C phase.

The McMillan model has recently been extended to liquid crystals of disc-like molecules (Kats 1978; Feldkamp *et al* 1981; Chandrasekhar 1983; Chandrasekhar *et al* 1984). The translational order parameter now describes a two-dimensionally periodic

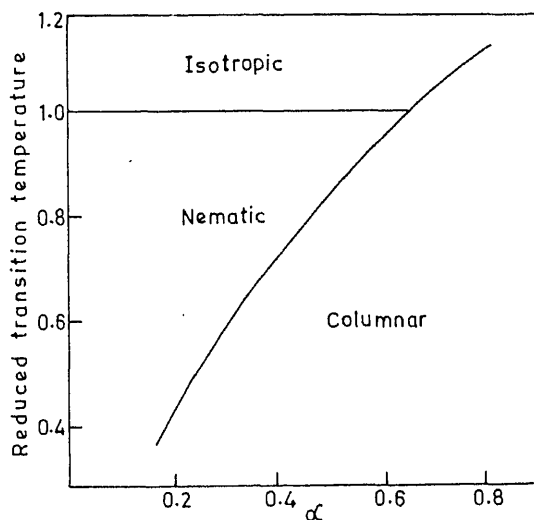


Figure 4. Theoretical diagram showing the hexagonal, nematic and isotropic phase boundaries. All the transitions are of first order (Feldkamp *et al* 1981; Chandrasekhar *et al*

(Feldkamp *et al* 1981; Chandrasekhar 1983; Chandrasekhar *et al* 1984) (figure 4). On the other hand, for a biaxial face-centered rectangular lattice (with axial ratio $b/a \neq 3^{1/2}$) the nature of the phase diagram depends on the value of b/a (Chandrasekhar 1983; Chandrasekhar *et al* 1984). When b/a departs only slightly from $3^{1/2}$, the behaviour is very similar to the hexagonal case. Interpreting α to be a measure of the chain length as in McMillan's model, the phase diagram is in broad agreement with the trends exhibited by the hexa-*n*-alkoxy-benzoates of triphenylene. For greater asymmetry of the lattice, the theory predicts the possibility of a columnar-biaxial smectic *A* transition as well. Evidence of a smectic phase in bis-(*p*-n-decylbenzoyl)methanato copper(II), a disc-like molecule, has been reported very recently (Ribeiro *et al* 1984). Thus this simple model serves to illustrate that the origin of the two-dimensional translational order in the columnar phase is similar to that of the one-dimensional order in the smectic *A* phase of rod-like molecules in so far as the attraction between the aromatic cores and the role of the end chains are concerned.

3. Some special interactions

In this section we discuss some special types of molecular interactions in liquid crystals which give rise to remarkable effects of fundamental significance, *eg*, flexo-electricity, ferroelectricity, reentrant phenomena, etc.

3.1 Flexo-electricity

If the molecule possesses shape polarity as well as a permanent dipole moment, then a splay or bend deformation may polarize the nematic medium, or conversely an electric field may induce a deformation (Meyer 1969; figure 5). This property is known as flexo-

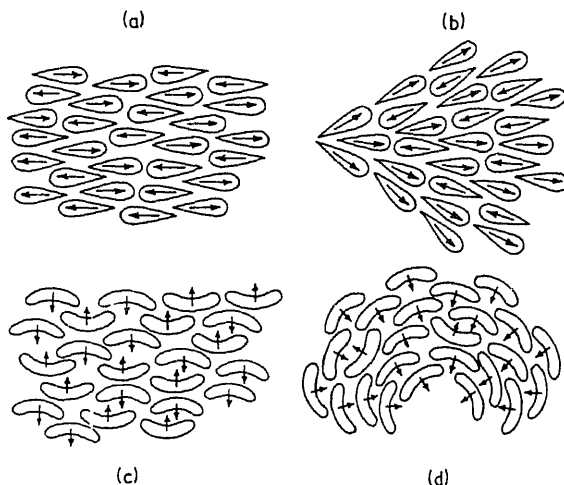


Figure 5. Meyer's model of flexoelectricity. The nematic composed of polar molecules is non-polar in the undeformed state (a and c) but polar under splay (b) or bend (d).

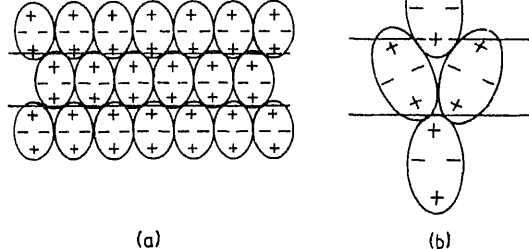


Figure 6. Schematic interpretation of the origin of flexoelectricity in an assembly of quadrupoles (Prost and Marcerou 1977): (a) the symmetry is such that there is no bulk polarization, (b) a splay deformation causes the positive charges to approach the upper plane and to be pushed away from the lower one. This dissymmetry gives rise to a dipole moment pointing upwards.

electricity. The mechanism may be generalised to include induced dipole moments as well. The effect may be looked upon as arising from a coupling of an electric field with a gradient of the director field, but additionally there may be another contribution which comes from a coupling of an electric field gradient with the director. The latter can be attributed to the quadrupole moments of molecules which need not even have shape polarity (Prost and Marcerou 1977). Figure 6 illustrates the physical picture of the origin of flexo-electricity in an assembly of quadrupoles.

The permanent dipolar contribution to the flexo-electric coefficient for pear-shaped molecules may be written as (Marcerou and Prost 1978; Derzhanski and Petrov 1979)

$$f = K_{11} \frac{\epsilon_{zz}^0 - \epsilon'_{zz}}{4\pi\alpha},$$

where ϵ_{zz}^0 is the static dielectric constant parallel to the director, ϵ'_{zz} that at a frequency just above the first relaxation (see §4.2), K_{11} the splay elastic constant and α a number relating to the shape polarity. Since $K_{11} \propto s^2$, where s is the order parameter, $f \propto s^2$ to a first approximation. Further, for frequencies beyond that of the relaxation, the permanent dipolar contribution to f is zero.

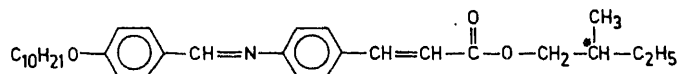
The quadrupolar contribution is (Marcerou and Prost 1978; Derzhanski and Petrov 1979)

$$f \approx -\frac{2}{3}ns\theta_a$$

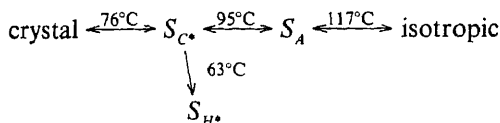
where n is the number of molecules/cc, and θ_a the quadrupole moment. Thus, in this case $f \propto s$ and moreover it will not have the frequency dependence of the permanent dipolar contribution. From experiments in the N as well as S_A phases, it has been shown that it is the quadrupole effect that is most common (Prost and Pershan 1976; Marcerou and Prost 1980), f being usually $\approx 10^{-4}$ esu.

3.2 Ferroelectricity

Ferroelectricity in liquid crystals was first demonstrated by Meyer *et al* (1975; see also Meyer 1977) in the S_C and S_H phases of DOBAMBC,



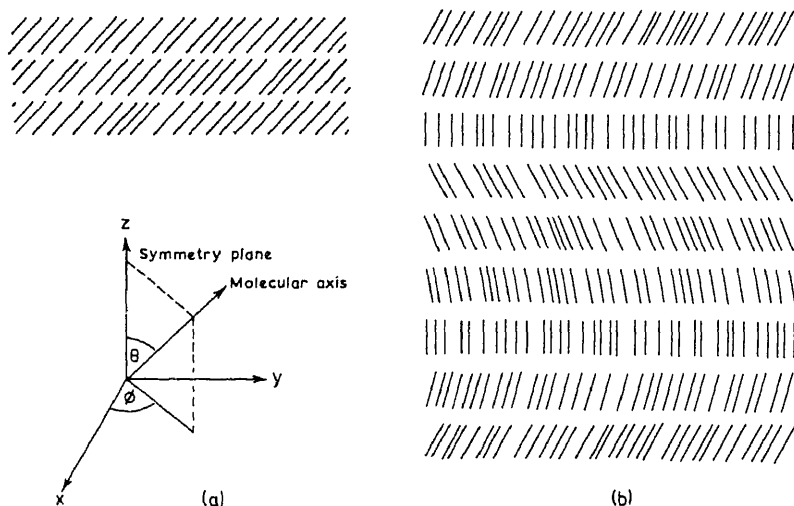
which shows the following transitions:



In the S_A phase, the molecules (which are not only chiral but also have a non-zero dipole moment) are arranged normal to the layers. Since there is no 'head-to-tail' ordering (the director being apolar) there is no polarization normal to the layers. Further, since the molecules are rotating about their long axes the transverse component of the dipole moment is averaged out and there is no net polarization parallel to the layers.

In the S_{C^*} phase the molecules are tilted and their rotation about their long axes is biased. The symmetry plane of the ordinary S_C structure (figure 7a) is now absent because the molecules are chiral. The only symmetry element left is a two-fold rotation axis parallel to the layers and normal to the long molecular axis. This allows the existence of a permanent dipole moment parallel to this axis. Thus in S_{C^*} each layer is spontaneously polarized. The value of this polarization is very small, about $3 \times 10^{-8} \text{ C/cm}^2$ as compared with $5 \times 10^{-6} \text{ C/cm}^2$ for KH_2PO_4 . In terms of the dipole moment this turns out to be only ≈ 0.25 debye/molecule. The tilt and the polarization directions rotate from one layer to the next (figure 7b). This implies that there is constant bend around the z -axis which leads to a flexo-electric contribution to the polarization (Durand and Martinot-Lagarde 1980).

When an electric field E is applied normal to the helical axis, the helix gets distorted; above a critical field E_c , it is completely unwound and the sample is poled with the molecules tilted along a preferred direction normal to E . Since this unwinding involves the rotation of the tilt direction, the response is damped by the rotational viscosity of the fluid. Therefore E_c increases with frequency. For the same reason the dielectric



Liquid crystalline ferroelectrics may be classified as 'improper' ferroelectrics. Both the tilt angle θ and the polarization P go to zero continuously as the temperature is raised to the $C^* - A$ transition point (T_{C^*A}). Actually T_{C^*A} is itself the Curie point. This coupling between P and θ produces a divergent component in the dielectric constant. It is expected that for $T < T_{C^*A}$ there is in addition to a *soft* mode, a symmetry recovering *Goldstone* mode. Attempts have been made to identify these modes from dielectric relaxation measurements (Garoff and Meyer 1977; Hoffmann *et al* 1978; Levstik *et al* 1979; Zeks *et al* 1979; Martinot-Lagarde and Durand 1981).

The pyroelectric behaviour of these ferroelectric smectics has been studied (Yu *et al* 1976). The pyroelectric coefficient $\gamma(T) = dP_s/dT$ increases with increase of temperature and near T_{C^*A} it is $\approx 2 \times 10^{-9} \text{ C cm}^{-2} \text{ deg}^{-1}$, comparable to the values for solid pyroelectrics. Away from T_{C^*A} , $\gamma = 2 \times 10^{-11} \text{ C cm}^{-2} \text{ deg}^{-1}$. The pyroelectric response to a heat pulse exhibits an exponential decay and the time constant is equal to the relaxation time of the dipoles responsible for the spontaneous polarization (Yu *et al* 1976; see also Blinov *et al* 1979).

3.3 *Re-entrant phases and the polymorphism of smectic A*

If the nematic is composed of molecules having a strong longitudinal dipole moment (as will be the case if the molecular end group is CN or NO₂) neighbouring molecules tend to be antiparallel. However, since the mesophase is fluid there can be no long range antiparallel order. The concept of antiparallel near-neighbour correlations (or *antiferroelectric short range order*) was proposed some years ago and its implications were discussed on the basis of the Bethe-Peierls cluster approximation (Madhusudana and Chandrasekhar 1973b; Madhusudana *et al* 1977). An important prediction of the theory is that the mean dielectric constant should increase by a few per cent on going from the nematic to the isotropic phase because of a decrease in the anti-parallel ordering at the transition, and this is borne out by measurements on a number of compounds (Schadt 1972; Ratna and Shashidhar 1976; Bradshaw and Raynes 1981; for a complete list of references, see Chandrasekhar 1984). Neutron diffraction studies on isotopically substituted cyano-compounds have confirmed that the nearest neighbours do indeed prefer to be antiparallel (Leadbetter *et al* 1979a).

A remarkable consequence of this type of antiparallel correlation was discovered by Cladis (1975) in binary mixtures of cyano-compounds. Over a range of compositions, the sequence of transitions on cooling was as follows:

$$I \rightarrow N \rightarrow S_A \rightarrow N \rightarrow \text{solid}.$$

The lower temperature N phase is referred to as the *reentrant nematic* phase (N_R). Examples of more complex behaviour are now known, but we shall first consider this simple type of reentrance. Some relevant experimental facts pertaining to this type of reentrant behaviour are (i) the smectic A phase is a partially bilayer structure, designated as A_d (see figure 9), its layer spacing varying only *very slightly* with temperature or pressure (Guillon *et al* 1978; Chandrasekhar *et al* 1980a, b; Raja and Shashidhar 1984) and (ii) the dielectric anisotropy increases as the sample is cooled from N through A_d into the N_R phase (Ratna *et al* 1980).

From the molecular point of view, only an approximate, qualitative explanation of

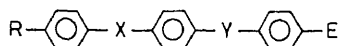
(a)

(b)

Figure 8. Schematic representation of (a) a dimer unit consisting of two antiparallel molecules, (b) the mechanism of destabilization of the smectic A phase (Cladis 1980).

reentrant behaviour has been possible. The basic idea underlying the molecular model is that because of the antiparallel correlations the molecules form dimers, which are assumed to be somewhat bulgy in the middle (figure 8a). Once the smectic phase is formed the bulgy parts are lined up in a plane, but the alkyl chains cannot fill the rest of the space. With increasing dimer formation (ie with decreasing temperature) and also possibly with the stiffening of the end chains, the packing becomes so unfavourable that the A_d phase is destabilized and the nematic reenters (figure 8b). The elements of the model were proposed by Cladis (1980, 1981) and Cladis *et al* (1981), but a more complete theoretical discussion involving attractive forces and hard core repulsions has been presented by Longa and de Jeu (1982), who showed that there can indeed be a lower temperature nematic phase. Qualitatively this is satisfactory. However, antiferroelectric short range order is a statistical effect, and to look upon the system as a sum of two extreme situations, the perfectly paired dimer with the dipoles compensated and the completely unpaired monomer with the full value of the dipole moment is a rather gross approximation. For example, the model assumes that there is a substantial increase in the dimer concentration with decreasing temperature. If this were so the smectic A layer spacing should increase markedly and the dielectric anisotropy should drop appreciably with decreasing temperature (see Chandrasekhar 1984). Both these predictions are at variance with the experimental facts. One may conclude, therefore, that the appearance of the reentrant phase involves much more subtle structural changes than expected from the current molecular treatments of this phenomenon. Essentially the same conclusions have been drawn from high resolution x-ray studies by Kortan *et al* (1984) who found no detectable change in the lateral intermolecular spacing or in the in-plane correlations in the N , A_d and N_R phases.

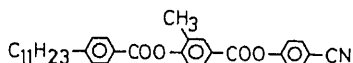
As mentioned earlier, much more complex examples of reentrance have now been found, notably by the Bordeaux group (for recent reviews see Hardouin *et al* 1983 and Tinh 1983). Closely related to this is another interesting effect, *viz*, the occurrence of different types of smectic A and of smectic A -smectic A transitions. It emerges that both reentrant behaviour and smectic A polymorphism are extremely sensitive to the molecular structure. We illustrate this by considering the properties of pure 3-benzene-
ring compounds having the structural formula given below. From the data reported to date, the compounds fall into 4 distinct types, the arrows representing the directions of the longitudinal components of the dipole moments of the bridging groups X and Y.



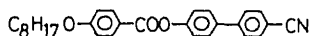
	X	Y	E	
Type I	→	→ or ← or non-polar	CN	Reentrant nematic
Type II	→	→ or ← or non-polar	NO ₂	No reentrance No <i>A-A</i> transition
Type III	←	←	CN	<i>A-A</i> transitions, no reentrance
Type IV	←	←	NO ₂	Reentrance and <i>A-A</i> transitions

Examples:

Type I (a) $I \rightarrow N \rightarrow A_d \rightarrow N_R$

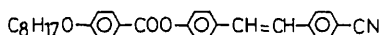


Madhusudana *et al* 1979

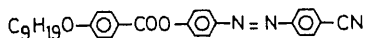


Hardouin *et al* 1979a

(b) $I \rightarrow N \rightarrow A_d \rightarrow N_R \rightarrow A_1$

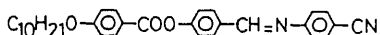


Hardouin *et al* 1979b

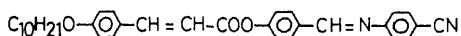


Heppke *et al* 1980

(c) $I \rightarrow N \rightarrow A_d \rightarrow C \rightarrow N_R$

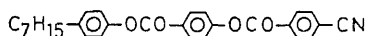


Weissflog *et al* 1980

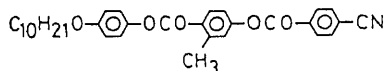


Tinh *et al* 1982

Type III $I \rightarrow N \rightarrow A_d \rightarrow A_2$

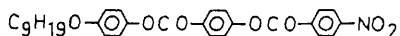


Hardouin *et al* 1981



Madhusudana *et al* 1982

Type IV (a) $I \rightarrow N \rightarrow A_d \rightarrow N_R \rightarrow A_d \rightarrow N_R \rightarrow A_1 \rightarrow \tilde{C} \rightarrow A_2 \rightarrow C_2$



Tinh *et al* 1982; Shashidhar *et al* 1985

(b) $I \rightarrow N \rightarrow A_1 \rightarrow \tilde{A}$

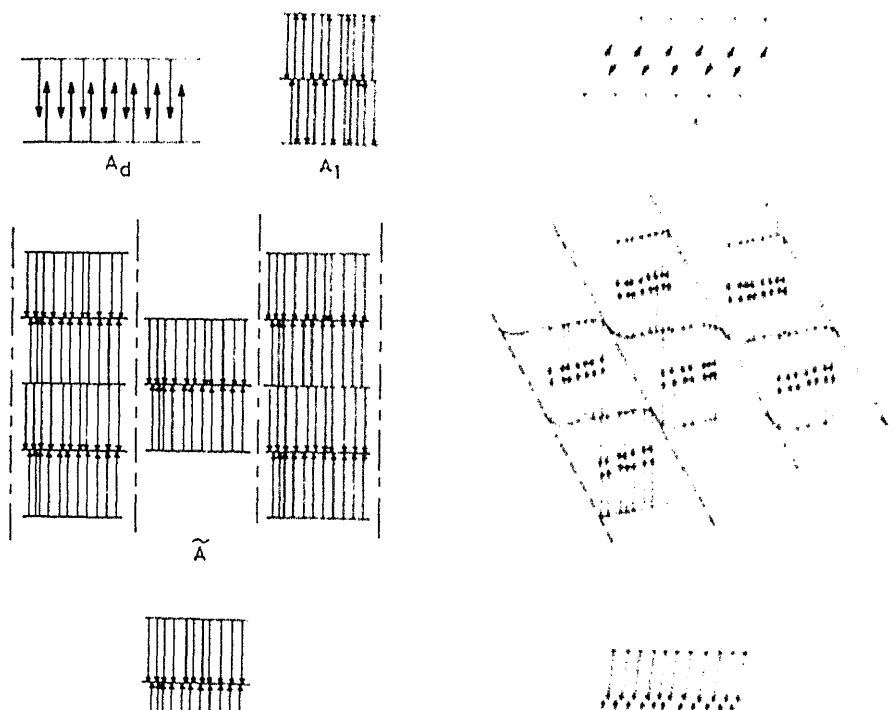
It is worth mentioning that type IV(a) is an example of a compound showing three nematic, four smectic *A* and two smectic *C* phases! Schematic representations of the structures of the different *A* and *C* phases identified to-date are given in figures 9 and 10 respectively.

Needless to say, we are nowhere near explaining these facts from a molecular theoretical point of view (though a beginning has been made by Longa and de Jeu 1983a, b, to try and develop a molecular model to account for the different types of *S_i* phases). From the phenomenological point of view, the different phases can be described as arising from a competition between two *incommensurate* lengths, one of them owing its existence explicitly to the antiferroelectric short range order (see Prost and Barois 1983).

Reentrant behaviour has been observed in mesophases of disc shaped molecules as well (Destrade *et al* 1981b). The higher homologues of the hexa-substituted esters of trixene (figure 3c) show the following sequence of transitions on cooling

$$I \rightarrow D_h \rightarrow N_D \rightarrow D_r \rightarrow D_h \rightarrow \text{crystal}.$$

An important point to be noted here is that the molecule is non polar. Based on the x-ray analysis of the crystal structure of a similar disc-shaped mesogen—a triphenylene compound (Cotrait *et al* 1979)—it has been suggested that the molecules are associated



in pairs in each column and that changes in this association are responsible for this effect.

3.4 The induced smectic phase

Another interesting example of a special type of molecular interaction in liquid crystals concerns the *induced* smectic phase, *ie*, the appearance of a smectic phase in the temperature-concentration diagram of a binary mixture even though neither component shows this phase in the pure state. This effect occurs most commonly in mixtures with one component having a strongly polar terminal group and the other a non-polar terminal group (Park *et al* 1975; Oh 1977; Griffin *et al* 1978; Bock *et al* 1978; for a complete list of references see Chandrasekhar 1984). An example of a phase diagram showing an induced S_A phase is presented in figure 11. Evidently, dipole-induced dipole interactions play a part in the phase induction. There is also evidence of charge transfer complex formation, the polar molecule acting as the acceptor and the other as the donor (Park *et al* 1975; Sharma *et al* 1980; Araya and Matsunaga 1981). Recently, however, phase induction has been observed in other types of mixtures (Goodby *et al* 1984; Madhusudana *et al* 1984; Suresh 1983). For example mixtures of two cyano-compounds have been found to give rise to an induced S_c phase (Goodby *et al* 1984; Madhusudana *et al* 1984). Thus no generalisations are possible as yet and the precise nature of the molecular interactions and correlations responsible for promoting phase induction is not quite clear.

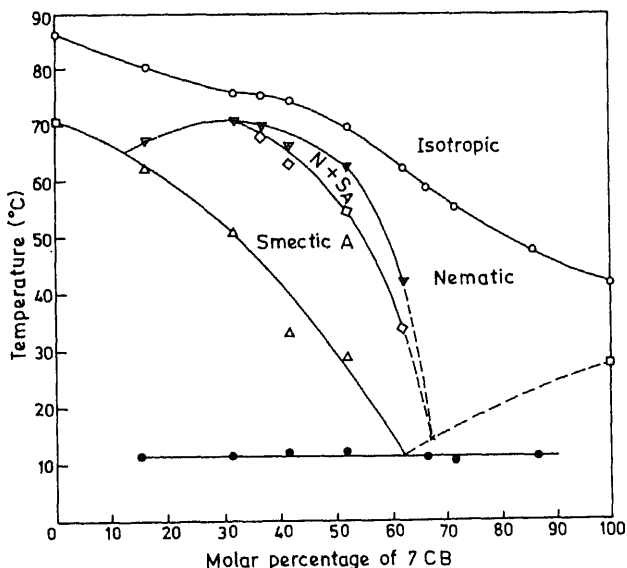


Figure 11. Phase diagram of binary mixtures of (2-hydroxy)-p-ethoxybenzylidene-p'-methoxyaniline and 7 CB.

4. Molecular dynamics

4.1 Introductory remarks

A complete analysis of the dynamics of molecular motion in the mesophases is a rather complex problem. To begin with, the molecule itself is by no means a rigid rod; there are bonds, often even in the central aromatic core, which allow reorientation of its different parts, and in particular its end chains, which as we have remarked earlier play an important role in determining the mesomorphic properties, are quite flexible. Besides, the molecule as a whole undergoes rapid reorientation about its long axis, though the rotation is probably not completely free for the individual molecule even in the uniaxial nematic and smectic *A* phases because of the absence of cylindrical symmetry in the molecular shape and the existence of an appreciable degree of short range order. It also executes a much slower and highly hindered rotational (or flipping) motion about its short axes. In addition to all this there are collective motions which depend very specifically on the structure of the mesophase. Thus molecular dynamics in liquid crystals is determined in a complicated way by both intra- and inter-molecular interactions and of course these interactions are strongly temperature dependent.

X-ray diffraction can be used to obtain the molecular distribution functions, but as is well known it does not lend itself to distinguishing between static and dynamic phenomena. In order to gain information on molecular motions, one has to resort to other methods, *eg*, dielectric dispersion, neutron diffraction, Raman, IR, NMR relaxation and light scattering. We shall now review the application of these different techniques.

4.2 Dielectric dispersion

As all liquid crystals have orientational order, it is clear that the molecular reorientations about the short axis of the rod-like molecule will be strongly hindered. One can readily visualise two minima in the potential energy curve (bearing in mind that the director is *apolar*) and the molecule can therefore execute a head-to-tail flipping motion. Thus, if the molecule has a component of the dipole moment parallel to its long axis, a relaxation of $\epsilon_{\parallel}$, the dielectric constant measured parallel to the director, takes place at relatively low frequencies. The first observation of this low frequency relaxation was made in several homologues of the PAA series by Maier and Meier (1961) who correctly attributed it to the influence of the nematic potential. Figure 12 gives the experimental curves for the sixth homologue. Subsequently, Axmann (1966a) made more detailed measurements on several compounds and used the Cole-Cole plot to depict the results. Since then a large number of studies have been made, in pure compounds as well as mixtures, both in the *N* and *S_A* phases (de Jeu 1978). The relaxation of $\epsilon_{\parallel}$ usually lies in the MHz-frequency range, as for the biphenyls, Schiff bases, etc, but for certain esters the viscosities are higher and the relaxation frequencies are lower. At temperatures much below T_{NI} , relaxation frequencies as low as a few kHz have been observed (de Jeu *et al* 1972).

Meier and Saupe (1966) and Martin *et al* (1971) defined a retardation factor $g = \tau_1/\tau_0$ where τ_1 is the observed relaxation time of $\epsilon_{\parallel}$ in the *N* phase and τ_0 the ordinary Debye relaxation time (the value extrapolated from the isotropic phase). Extending the Debye model, and assuming that the molecule has only μ_1 , the longitudinal component of the dipole moment, these authors were able to relate the retardation factor g with the orientational order parameter S and the temperature dependence of the order parameter.

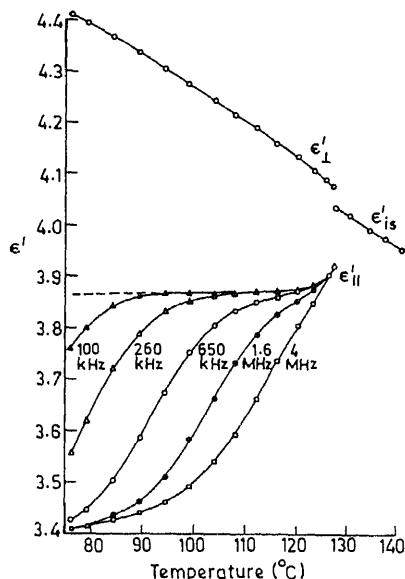


Figure 12. The real part of the principal dielectric constants $\epsilon'_{\parallel}$, $\epsilon'_{\perp}$ in the nematic phase and ϵ'_{is} in the isotropic phase of 4,4'-di-*n*-hexyloxyazobenzene at different frequencies between 100 kHz–4 MHz. $\epsilon'_{\parallel}$ shows a strong dispersion whereas $\epsilon'_{\perp}$ and ϵ'_{iso} do not. (From Maier and Meier 1961a, b, reproduced by permission of Verlag der Zeitschrift für Naturforschung.)

able to account for the observed dispersion in cyanobiphenyl compounds in which the dipole moment lies practically along the major molecular axis. However, the absolute value of g estimated on the basis of this theory turns out to be somewhat greater than that obtained from the Maier-Saupe theory using the observed value of the order parameter s . For example for PAA at 121°C, $g \approx 100$ and $q = 0.22$ eV, whereas the Maier-Saupe theory gives $q = 0.14$ eV. The difference may be attributed to the fact that the dielectric relaxation process is very sensitive to the short-range orientational order which is much stronger than the long-range order measured by s , and which is neglected completely in the mean field theory.

Nordio *et al* (1973a) have pointed out that the correlation time measured in the isotropic phase of PAA from NMR relaxation data (see §4.5) is $\approx 10^{-10}$ sec while dielectric relaxation in the same phase gives $\tau_0 \approx 3.2 \times 10^{-11}$ sec. They have attributed this discrepancy to the reorientation of the methoxy groups contributing to the dielectric data and have found that in fact $g = 11.5$ and not ≈ 100 as assumed by earlier authors. The strength of the nematic potential thus obtained would agree better with the mean field result than the earlier estimates.

There have been other theoretical approaches to the problem of dielectric relaxation. Nordio *et al* (1973b) have treated it by evaluating the time correlation function of the fluctuating molecular dipole components taking into account the effects of the diffusion tensor. They have used higher order terms of the nematic potential in the theory, and have included both μ_l and μ_t , the longitudinal and transverse components of the molecular dipole moment. Luckhurst and Zannoni (1975) have also developed a

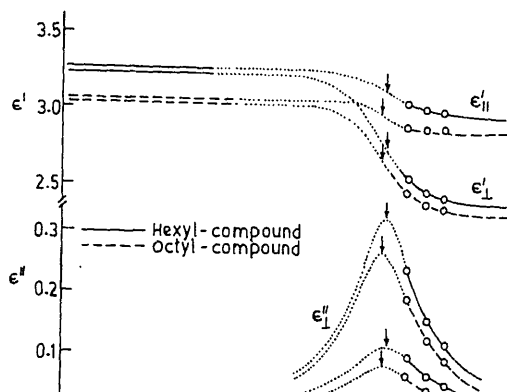
Kresse (1981) have proposed a rigid ellipsoid diffusion model to describe the dielectric relaxation in the isotropic phase of liquid crystals.

As remarked by Luckhurst and Yeates (1976) all these theories assume that the orientational motion is diffusional, whereas, in point of fact, changes in molecular orientation can occur through large angle jumps. Moreover, as discussed in earlier sections, the assumption that the molecule is rigid and cylindrically symmetric is certainly not correct. No attempts appear to have been made to take into account these factors in developing a general theory of dielectric relaxation.

The relaxation frequency for $\epsilon_{||}$ in the N phase may be expected to decrease, and the corresponding activation energy increase, with increasing molecular length. This has been confirmed by the systematic experiments of Schadt (1972) and Bata *et al* (1977). Indeed even an odd-even effect has been found for the relaxation frequency of successive members of a homologous series (Ratna and Shashidhar 1978).

For the vast majority of compounds that show both N and S_A phases, regardless of whether they are positive or negative dielectric anisotropy materials, it is found that the activation energy for low frequency dielectric relaxation is less in S_A than in the N phase (see Chandrasekhar 1984). In other words, the reorientation of the molecule about its short axis appears to be easier in the S_A phase. On the other hand, the activation energy in the N_R phase is much higher than in the N phase (Ratna *et al* 1980). The reason for the lower activation energy in S_A is still far from clear.

Though in principle $\epsilon_{||}$ also contains some information on rotations about the long molecular axis, such a motion would more directly influence the relaxation of $\epsilon_{\perp}$. If $\mu_t = 0$, i.e. $\beta = 90^\circ$ (where β is the angle which the net dipole moment makes with the long axis) both $\epsilon_{||}$ and $\epsilon_{\perp}$ should relax at about the same frequency, as is found to be the case for 4,4'-di-*n*-alkoxyazobenzenes (Axmann 1966b) (figure 13). The relaxation time for these compounds is $\approx 4 \times 10^{-11}$ sec, which corresponds to the rotational time of the (alkoxy) end groups which carry the dipole moment. If $\beta \neq 90^\circ$, $\epsilon_{||}$ shows an additional lower frequency relaxation which, as we have already discussed, comes from



axis, the rotation of the end groups and other mechanisms. For example, measurements (Parneix *et al* 1975) on eutectic mixtures of two isomers of *p*-methoxy-phenylazoxy-*p*'-butylbenzene over the frequency range 1 Hz–26 GHz, show a distribution of relaxation times for $\epsilon_{\perp}$. In the MHz region, only $\epsilon_{\parallel}$ shows a relaxation. At high frequencies, 0.5–0.7 GHz, both $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ show a relaxation with an activation energy of ≈ 0.2 eV. This relaxation persists in the isotropic phase also and is attributed to the rotations of the molecules about the long axis. Further, a feeble relaxation is found at ≈ 3 GHz for $\epsilon_{\perp}$, probably arising from the rotation of the end group.

In a recent study of MBBA (4-methoxybenzylidene-4'-butylaniline) up to 18 GHz, Buka *et al* (1979a) have found a high frequency relaxation of $\epsilon_{\parallel}$ at 10^9 Hz which arises from reorientation of the *transverse* component $\mu_{\perp}$. $\epsilon_{\perp}$ also has two relaxations, at $\approx 10^9$ and $\approx 10^{10}$ Hz, the lower frequency one being attributed to the reorientation of the entire molecule and the higher frequency one to internal rotations of the methoxy group.

The case of alkyl cyanobiphenyls (*n*CB) is particularly interesting since the dipole moment lies practically along the long molecular axis and contributes to the dispersion of both $\epsilon_{\parallel}$ and $\epsilon_{\perp}$. Davies *et al* (1976) found in the case of 7CB that while the dispersion of $\epsilon_{\parallel}$ as well as ϵ_{iso} are characterised by essentially a single relaxation time, the dispersion of $\epsilon_{\perp}$ is characterised by a distribution of relaxation times (around 2×10^{-9} sec). According to the theory of Martin *et al* (1971) the librations of the molecules about the director contributes to the relaxation of $\epsilon_{\perp}$ at higher frequencies. Since the molecular order and hence the local field is not well defined in the perpendicular direction, and also since the barrier height in this direction is small, a wide range of individual dipole reorientation rates is allowed. Davies *et al* (1976) concluded that the data can be fitted satisfactorily to the theory.

A somewhat more detailed study has since been carried out by Druon and Wacrenier (1977, 1978) and Wacrenier *et al* (1981) on 8 CB, and on 7 CB by Lippens *et al* (1977) in the S_A , N and I phases. In the I phase a relaxation occurs at ≈ 25 MHz which indicates that the rotations are due to clusters rather than individual molecules. The relaxation spectrum of $\epsilon_{\perp}$ includes frequencies below 10 MHz, which again is evidence of molecular associations. The spectrum has been decomposed into three regions around 10 MHz, 100 MHz and 700 MHz (figure 14). The authors have concluded that while the theory of Martin *et al* (1971) can approximately explain the occurrence of the two higher frequency relaxations, it cannot account for the lowest frequency relaxation at ≈ 10 MHz. They have ascribed the low frequency relaxation to associated groups deviating from the director with a short life time of the order 10^{-7} sec. This hypothesis has been incorporated in the Martin *et al* model to account for the low frequency relaxation. The short-range order effect has been estimated to extend over 100–200 molecules. An interesting consequence of this type of short lived association is that in a small range of frequencies, just beyond that corresponding to the relaxation of $\epsilon_{\parallel}$ and till the lowest frequency of relaxation of $\epsilon_{\perp}$, the dielectric anisotropy of 8 CB is *negative*, even though the molecules have no net dipole moment perpendicular to the long axis (figure 15).

7CB and 7OCB (hepoxy cyanobiphenyl) have again been studied very recently by

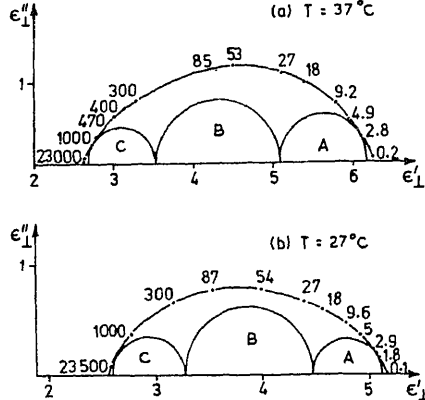


Figure 14. Cole-Cole plot for $\epsilon_{\perp}$ in (a) the nematic and (b) the smectic A phases of 8CB. The frequencies are in MHz. (From Druon and Wacrenier 1978, reproduced by permission of Masson.)

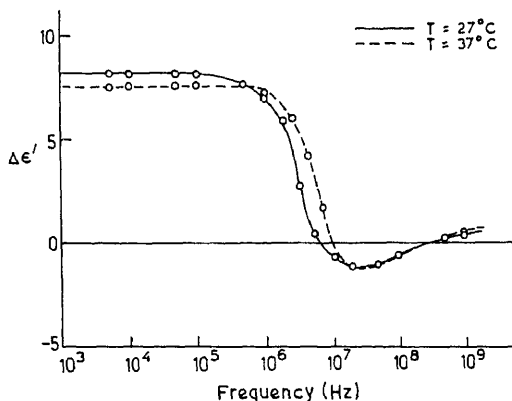


Figure 15. Dispersion of the dielectric anisotropy $\Delta\epsilon'$ in the nematic (at 37°C) and smectic A (at 27°C) phases of 8CB. (From Druon and Wacrenier 1977, reproduced by permission of Commissions des Publications Française de Physique.)

Buka *et al* (1979b) upto 18 GHz. Interestingly, they have observed two relaxations for $\epsilon_{\parallel}$, the second one occurring at $\approx 10^9$ Hz in both cases (figure 16). This high frequency feature which occurs in the isotropic phase also has been attributed to partial reorientation within short-range ordered groups. In the $\epsilon_{\perp}$ studies, they observed only one broad absorption band and did not try to resolve it further into different relaxation frequencies. Moreover, in 7 OCB, they did not find any evidence for internal rotation of the heptoxy group. Price and Evans (1980) have tried to explain the high frequency relaxation of $\epsilon_{\parallel}$ in 7 CB theoretically by developing a model of Brownian motion with a superimposed pairwise orientational interaction potential. The numerical calculations

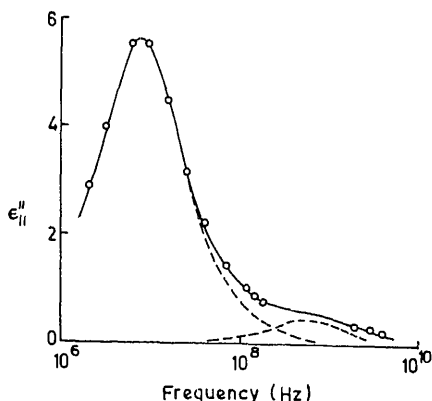


Figure 16. Dielectric absorption ϵ'' in 7CB. Circles denote the experimental data, the broken curves the two resolved components whose sum is represented by the solid curve. (From Buka *et al* 1979b, reproduced by permission of Gordon & Breach Science Publishers.)

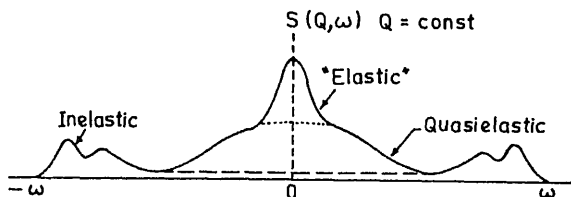


Figure 17. Schematic representation of the incoherent neutron scattering law $S(Q, \omega)$ at constant wavevector Q . The contribution to the elastic regime comes mainly from the translational motion, to the quasielastic regime from the translational and rotational motions, and to the inelastic regime from the vibrational, translational and rotational motions (Leadbetter and Richardson 1979).

4.3 Incoherent quasielastic neutron scattering

Neutron scattering is particularly suited to the study of rapid motions of the molecule and its constituent parts in condensed systems since the wavelengths of the neutrons used are of the order of molecular dimensions and yet at the same time their energies are low (1 Å corresponds to an energy of about 0.08 eV). The technique has been applied to liquid crystals for over a decade, but the high resolution work necessary for a proper analysis of the data has been undertaken only in the past four or five years. We refer the reader to a review by Leadbetter and Richardson (1979) for a discussion of the theoretical background and the scope of the technique. We present here only a brief summary of the basic ideas and the experimental results on liquid crystalline systems.

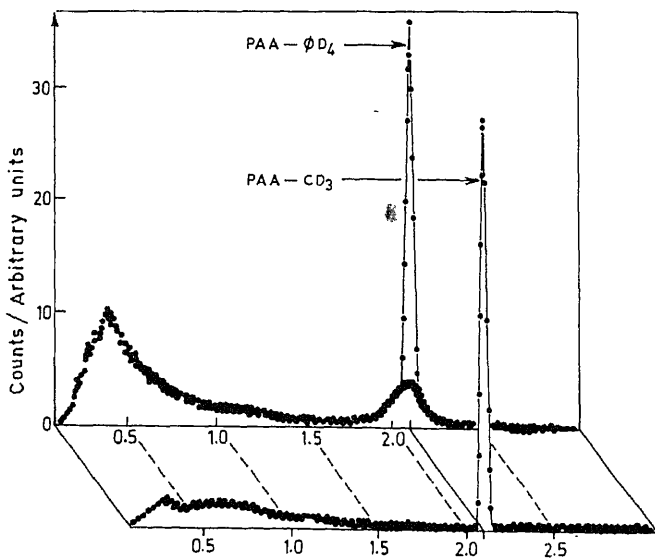
In principle, coherent inelastic neutron scattering data can be used to investigate collective modes (see §4.6). However, as far as the motions of individual molecules are

enables the translational diffusion constant to be defined. This is then used in the analysis of measurements at higher Q to determine the elastic incoherent structure factor (EISF) due to the rotational motion. The rotational correlation time may be derived directly from the width of the quasi-elastic component, though a complete description of the molecular dynamics requires detailed consideration of specific models.

Most mesogenic molecules contain many hydrogen atoms which have a very large incoherent scattering cross-section. By deuterating different parts of the molecule it is possible to study the motion of the undeuterated parts. Thus, from a comparison of the spectra of ring-deuterated and methyl-group deuterated versions of PAA (figure 18) Hervet *et al* (1976) found that even in the solid phase at $\approx 100^\circ\text{C}$ the methyl groups rotate about the O-C bond with a correlation time $\tau_R \approx 0.35 \times 10^{-12}$ sec and an activation energy ≈ 10 kJ/mole. From the spectrum in the nematic phase of d_6 -PAA, Janik *et al* (1980) concluded that the whole molecule reorients about the long axis with $\tau_R \approx 10^{-11}$ sec, while the benzene rings and O-CH₃ groups have intramolecular rotations with $\tau_R \approx 10^{-12}$ sec. Similar studies have been made Janik *et al* (1980) on d_{30} -HOAB (the seventh homologue of the PAA series) in both the N and S_C phases. It is found that the rotation of the phenyl rings is similar in the N and S_C phases but the end chain rotation is more rapid in the N phase.

A number of high resolution experiments have been carried out in recent years. Some typical spectra obtained from aligned samples are reproduced in figure 19. The broad conclusions of these studies are summarized below (Leadbetter and Richardson 1979; Rustichelli 1978; Volino and Dianoux 1979; Richardson *et al* 1980).

In the N phase the translational diffusion constants (D) are in the range 10^{-7} to



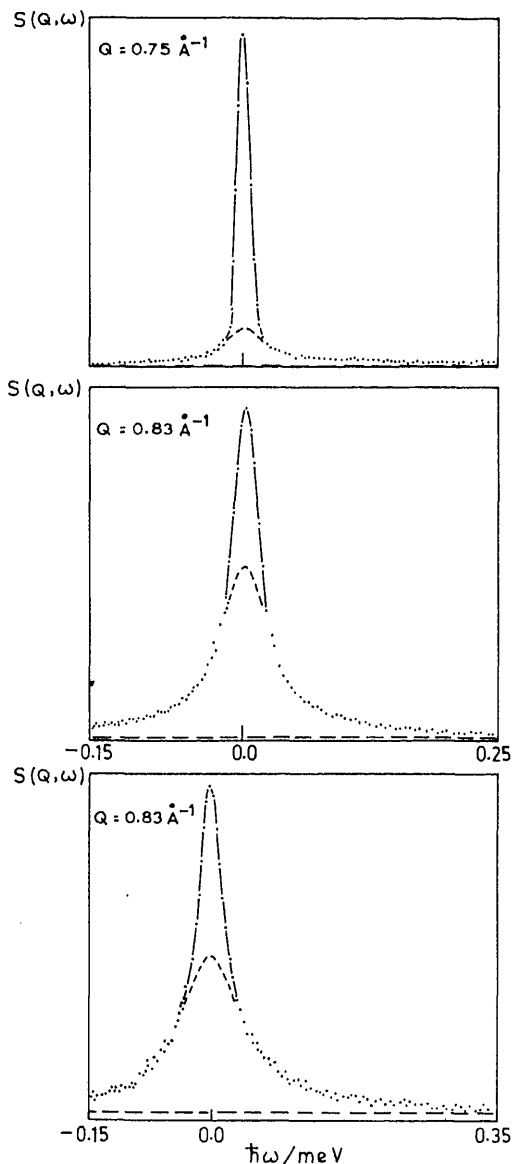


Figure 19. The quasielastic scattering law $S(Q, \omega)$ (in arbitrary units) of partially deuterated isobutyl 4-(4'-phenylbenzylidene amino)cinnamate. The data are shown for $Q \parallel a$ for three smectic phases, from top to bottom (i) S_E phase at 100°C (12 μeV FWHM resolution), (ii) S_B phase at 150°C (20 μeV FWHM resolution) and (iii) S_A phase at 172°C (20 μeV FWHM resolution). The curves show the experimental spectra separated into elastic and quasielastic components. The horizontal dashed lines represent a flat inelastic background. (From Leadbetter *et al* 1979b, reproduced by permission of Commissions des Publications Française de Physique.)

$5 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$, the values being, of course, temperature dependent. In S_A and S_C , D is of the same order of magnitude as in N ($\approx 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$) and is temperature dependent while in the more ordered smectic phases, *eg* S_A , S_B , S_C , $D \approx 5$

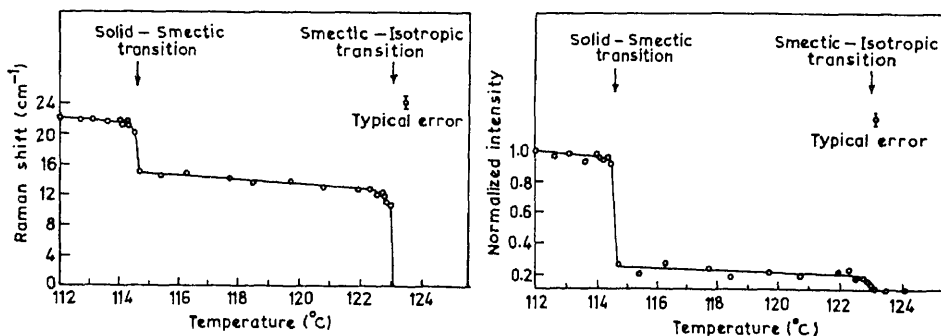
In N , S_A and S_C as well as in S_H and S_B , there is a rapid, uniaxial rotational diffusion about the long axis with a correlation time $\tau_R \approx 10^{-11}$ sec. In S_E , this becomes an overdamped libration of amplitude $\approx 30^\circ$ about the long axis. In S_E , S_B and S_A there is also a rapid localised (or 'bound') diffusive motion ($\tau \approx 10^{-11}$ sec and 1–2 Å RMS amplitude) perpendicular to the layers. In addition, in N and S_A there is a libration about the short axis on a time scale much slower than 10^{-10} sec.

4.4 Raman and infrared spectroscopy

While Raman and infrared spectroscopy may not be as powerful as some of the other techniques in elucidating molecular motions in liquid crystals, they do nevertheless yield valuable information. A large number of studies on mesogenic compounds have been reported (see reviews by Bulkin 1976; Chandrasekhar and Madhusudana 1972) the salient results of which will be summarized in this section.

4.4a Raman studies: Some interesting changes have been observed in the Raman spectra near the crystal-mesophase transition. For example, in PAA additional bands have been found in the $200\text{--}700\text{ cm}^{-1}$ region which have been attributed to new conformations of the molecules especially about the C–OCH₃ bonds in the N phase (Schnur *et al* 1972; Shibata *et al* 1976). The intermolecular Raman mode at $\approx 22\text{ cm}^{-1}$ which was observed in the crystalline phase of two smectogenic compounds was found to become weaker and shift towards lower frequencies in the S_A phase and disappear in the isotropic phase (Amer and Shen 1972) (figure 20). This as well as the increase in the line-widths of some higher frequency modes are considered to be due to the rotational freedom of the molecules in the fluid phases. Similar conclusions have been drawn about molecular rotational freedom in the N phase from a study of the low frequency Raman modes in azoxy compounds like PAA and PAP (Sakomoto *et al* 1974). It may be mentioned, however, that these low frequency modes were not observed in simple Schiff base compounds (Sakomoto *et al* 1974).

Vertogen and Fleury (1975a) found that in MBBA the temperature dependence of the bands due to the rigid benzylidene aniline group is substantially different from that of the bands due to the end alkyl group. The phase transition mainly affects the alkyl



chains. However in the N phase the melting of the chains is not complete (Destrade and Gasparoux 1975).

TBBA is a compound which exhibits many mesophases (Gray 1981; Demus *et al* 1980) and has been the subject of several Raman investigations. The Raman band at 19 cm^{-1} does not change much between the crystalline phases and the S_H (or according to the revised notation of Gray 1981 and Demus *et al* 1980, S_C) phase whereas it totally disappears in the S_C phase (Schnur and Fontana 1974; Schnur *et al* 1973; Dvorjetski *et al* 1975), though in a later study (Takase *et al* 1975, 1977) this band is reported to disappear in the S_H phase as well. This is supposed to indicate 'collective' rotations in the solid reducing in the S_C phase (and very likely also in the S_H phase) to more or less free rotations, probably involving a diffusive process (see §4.3). A broad peak at $\approx 130\text{ cm}^{-1}$ in the liquid crystalline phases has been attributed to the torsional motion of the butyl group relative to the phenyl group. There is also evidence of a rotational relaxation of the end chains in the crystal VIII phase which precedes the S_H phase (Fontana and Bini 1976).

The Raman spectra of the higher homologues of the PAA series reveal the accordion vibrations of alkyl chains in the solid phase (Schnur 1973). These disappear in the liquid crystalline phases, which means a partial 'melting' of the chains. Destrade *et al* (1976) have concluded that some intramolecular ordering exists in the end chains of nematogenic materials in the isotropic phase even far away from the N_I transition point, while such ordering is not detectable in the case of compounds which are not mesogenic.

From a study of the correlation functions for the Raman scattering associated with the $\text{C}\equiv\text{N}$ stretching mode of 8 OCB, Bulkin and Brezinsky (1978) have found that vibrational dephasing rather than 'tumbling' about the short molecular axis is primarily responsible for the bandwidth of this mode.

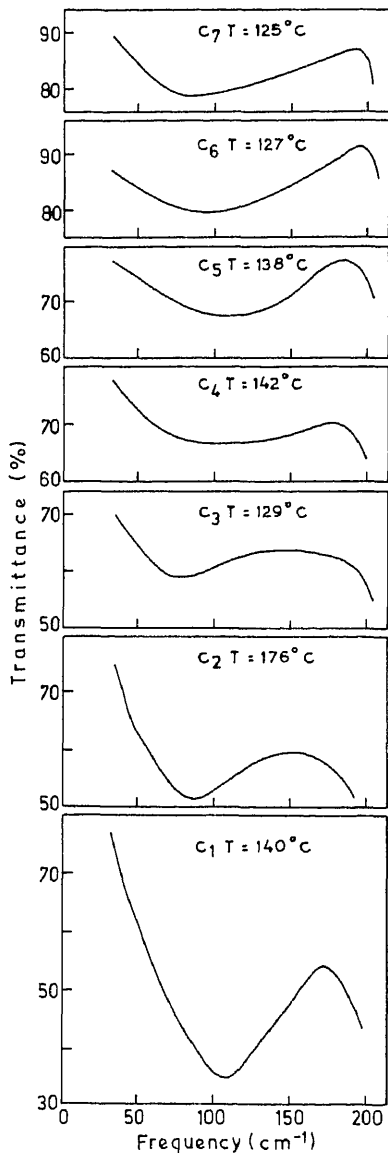
The low frequency Raman spectra of cholesteryl benzoate and stearate show practically no differences between the cholesteric and isotropic phases, while the smectic phase of the stearate compound has several features similar to those of the crystalline phase (Vertogen and Fleury 1975b).

As mentioned in §3.2, the molecular rotation about the long axis definitely cannot be 'free' in ferroelectric S_C , and an attempt was made by Takezoe *et al* (1979) to study the rotational bias by Raman scattering. However, the measurements were not accurate enough to come to any definite conclusions.

4.4b Infrared studies: The earlier studies were mainly in the near IR region and the linewidths of several bands were found to vary with temperature. This was ascribed to combination modes between the lattice vibrations and molecular vibrations/rotations. Attempts have been made to calculate from the widths of these bands the temperature variation of the potential barrier for molecular reorientation (Kirov and Simova 1973). However, it is not usually possible to assert that the motion is that of the entire molecule as these bands may arise from characteristic motions of sub-molecular groups only, and may even be due to more than one type of motion. For example, the far infrared band at 130 cm^{-1} observed in MBBA (and a similar band observed in the next higher homologue, EBBA, at 120 cm^{-1}) can be due to libration modes of the phenyl rings or due to the libration of the entire molecule about its long axis (Sciensinska *et al* 1974; Bulkin and Lok 1973; Demus *et al* 1973; Vertogen *et al* 1976).

initially thought to be of intermolecular origin (see Bulkin 1976 and Chandrasekhar and Madhusudana 1972). However, from a detailed and systematic investigation of this and its higher homologues which revealed that the band shifts to lower frequencies and also becomes wider with increasing chain length (figure 21), Venugopalan and Prasad (1979) have concluded that the main contribution to this band comes from the rotational motions of the end alkoxy chains.

From the near IR spectra of the seventh homologue of the PAA series (HOAB) which



exhibits both N and S_C phases, Lugomer (1974) has estimated the rotational correlation times of benzene rings to be 8×10^{-12} sec in the S_C phase and $4-5 \times 10^{-12}$ sec in the N and I phases. He has also concluded that the average angular rotational jump is $\approx 30^\circ$ in the smectic and $\approx 60^\circ$ in the other two phases. These rotational correlation times are expected to be at least an order of magnitude faster than that for the entire molecule. In the case of MBBA (Evans *et al* 1974) the correlation time for the rotation about the long axis in the isotropic phase is $\approx 7.5 \times 10^{-11}$ sec.

The order parameters of the rigid aromatic core and of hydrocarbon chains of several Schiff base derivatives have been determined in the N phase by the use of stationary and modulated infrared attenuated total internal reflection spectroscopy (Fringeli *et al* 1976). The hydrocarbon chains were found to be much less ordered than required by Marcelja's statistical theory (Marcelja 1974).

Fernandes and Venugopalan (1976) have found evidence for increased molecular rotations at the crystal- S_A transition point in CBOOA (4-cyanobenzylidene-4'-octyloxyaniline) by the disappearance of a combination mode at 518 cm^{-1} . The accordion mode of the alkyl chains at 296 cm^{-1} also disappears at this transition indicating a vibrational 'melting' of the chains in the mesophase.

Venugopalan *et al* (1977) have shown that the band centred at 476 cm^{-1} in the lower temperature solid phases of TBBA is broadened in smectic H and VI (or, according to the revised notation of Gray (1981) and Demus *et al* (1980), S_G and S_H respectively) (figure 22). This they have attributed to intramolecular reorientations of the butyl chain in the latter two phases. The mean correlation time of the reorientation is estimated to be 1.2×10^{-12} sec.

There have been comparatively fewer infrared studies on cholesteric compounds. Myasnikova and Corbatenko (1972) have found that the bands in the $1200-1330 \text{ cm}^{-1}$ region considered to be due to combination modes in six cholesteryl esters disappear at the crystal-cholesteric transition point. Evans *et al* (1975) have ascribed the broad 78 cm^{-1} band occurring in cholesteryl oleyl carbonate to a libration of the rigid part of the molecule about its long axis.

4.5 Nuclear magnetic relaxation

Nuclear magnetic relaxation is another very useful technique for investigating molecular dynamics. A great deal of work has been done particularly on the proton spin relaxation in nematics. However, most of the earlier experiments were confined to small frequency ranges and the results could not therefore be interpreted unambiguously. In the last four or five years Noack and co-workers, using field cycling techniques, have studied the dispersion of the proton spin relaxation time T_1 over a very wide frequency range (a few hundred Hz to 270 MHz) and have carried out a far more complete analysis of the different relaxation mechanisms than was possible previously. We shall limit our discussion to these recent studies as the earlier work has been adequately covered in a review article by Wade (1977) and Doane (1979).

Figure 23 shows the T_1 proton relaxation dispersion in the nematic phase of MBBA at two temperatures, one at 45°C (close to the N_I transition) and the other at 18°C in the

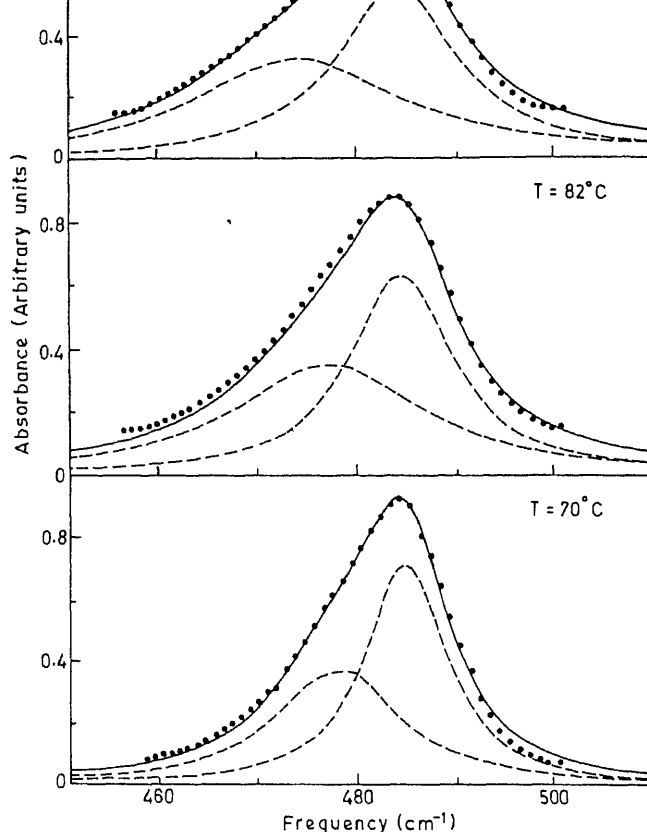


Figure 22. Infrared absorbance of TBBA in the S_G (95°C), S_H (82°C) and VII (70°C) phases in the 460–500 cm^{-1} range. Closed circles denote the experimental values. The uncertainty in the data is shown in the top trace. The broken curves denote least squares Lorentzian components and the solid curve represents the sum of the two components. (Venugopalan *et al* 1977, reproduced by permission of Gordon & Breach Science Publishers)

Assuming that the net relaxation follows a single exponential law, one may write (Abragam 1962)

$$1/T_1 = \sum_j (P_j/T_{ij})$$

where j stands for the given relaxation mechanism and P_j is the fraction of total number of protons in the molecule which contribute to this mechanism,

$$\frac{1}{T_{ij}} = \left(\frac{H^2}{T_{zj}} + \frac{H_L^2}{T_{dj}} \right) / (H^2 + H_L^2)$$

where H is the external field, and H_L the dipolar field due to neighbouring protons

the relaxation time for the Zeeman energy and T_{dj} that for the dipolar energy. Further,

$$1/T_{zj} = \frac{3}{2} \gamma^4 \hbar^2 I[I+1] [J_j^{(1)}(\omega) + J_j^{(2)}(2\omega)]$$

where I is the spin quantum number, γ the magnetogyric ratio and $R_j = T_{zj}/T_{dj}$ a characteristic ratio. Obviously, the effect of the dipolar relaxation is felt only when $H \approx H_L$, i.e. at low external fields. The $J(\omega)$ coefficients are determined by the dynamical processes involved, and in particular by the Fourier intensities at ω_L and $2\omega_L$ of the fluctuating field arising from molecular motions.

In isotropic liquids the main contributions come from intramolecular dipole-dipole interaction modulated by the rotational tumbling motion ($T_1 \approx \omega^2$) and the intermolecular dipolar relaxation caused by self-diffusion ($T_1 \approx \omega^{3/2}$). While both of these undoubtedly contribute to T_1 in liquid crystals, there is another mechanism unique to the mesophase, namely, the orientational fluctuations (OF) of the director. This is the most important collective motion in nematics. The continuum theory leads to the result that any thermal distortion of size q^{-1} is relaxed in a characteristic time τ_q given by

$$\tau_q^{-1} \approx Kq^2/\eta,$$

where K is an appropriate average of the curvature elastic constants of the nematic and η a viscosity. For $q^{-1} \approx 100 \text{ \AA}$, $\tau_q \sim \mu \text{ sec}$. Such distortions modulate the dipole-dipole interactions and contribute very strongly to the NMR relaxation in the MHz region with

$$J_q(\omega) = (2kT/Kq^2V) \tau_q/(1 + \omega^2\tau_q^2),$$

and taking into account the contribution to the relaxation time from distortions at all possible wavevectors q

$$\frac{1}{T_1} \approx A\omega^{-1/2} + B. \quad (1)$$

Thus the OF contribution to the relaxation rate shows an unusual frequency dependence. The theory, originally due to Pincus (1969) has been refined by other authors (Sung 1971; Ukleja *et al* 1976; Freed 1977) and extended to include the other mechanisms mentioned earlier, and possible couplings between the different relaxation modes. The most general theory is due to Freed (1977). It is obvious that a formidable amount of analysis is needed to work back from the relaxation data to the dynamical processes involved. As remarked before, the earlier measurements were limited to narrow frequency ranges and led to conflicting interpretations, but the recent wide frequency data of Graf *et al* (1977) make it somewhat easier to delineate the different contributions. Assuming that the OF, self-diffusion (sd) and molecular rotation (R) contributions are not coupled and taking the simplest theoretical expressions for $J(\omega)$ in each case, Graf *et al* reduced the number of parameters to be fitted to six, and found that the dependence of T_1 on temperature and frequency could be accounted for quite satisfactorily on this basis. The frequency variation of the three contributions are shown in figure 23. Two points may be noted: the contribution of T_{1R} is present only close to the transition, and T_{1sd} is strongly temperature dependent (the diffusion constant $D = 0.98 \times 10^{-7} \text{ cm}^2/\text{sec}$ at 18°C and $= 3.2 \times 10^{-7} \text{ cm}^2/\text{sec}$ at 45°C). A surprisingly good agreement was found with the computer fitted value of A of (1) and

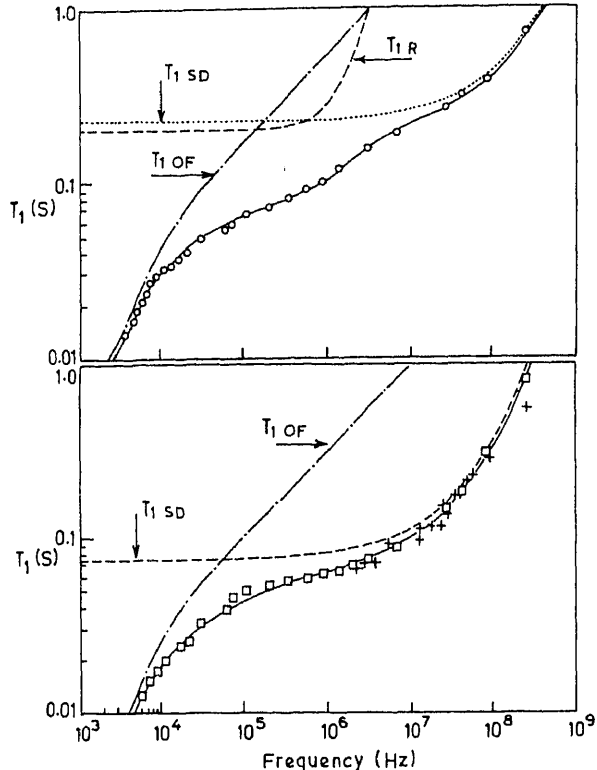


Figure 23. Dispersion of the proton spin relaxation time T_1 in nematic MBBA. Circles and squares are the experimental data of Graf *et al*, crosses the data of Vilfan and Blinc. Full lines represent the computer fitted curves taking into account the contributions of the orientational fluctuations of the director (OF), self-diffusion (SD) and molecular rotation (R). The individual contributions of T_{1OF} , T_{1SD} and T_{1R} are also shown. (From Graf *et al* 1977, reproduced by permission of Verlag der Zeitschrift für Naturforschung.)

In a later study on several homologues of the PAA series, Wolfel *et al* (1980) have given an alternative interpretation of the relaxation which occurs around 10^6 Hz. They have now attributed it to the critical fluctuations of the scalar order parameter s (or the magnitude of s) close to T_{NI} . The theory for this contribution had been worked out earlier by Freed (1977) in his general treatment of T_1 relaxation.

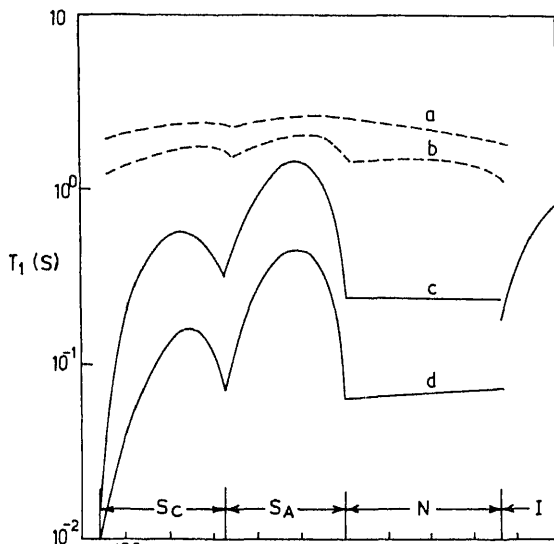
The scalar order parameter fluctuations can be treated in terms of the Landau-de Gennes theory (de Gennes 1974; Chandrasekhar 1977). The critical slowing down of this order parameter fluctuation as the temperature approaches T^* , a hypothetical second order N_I transition point slightly above the actual (first order) transition point T_{NI} , has been recently studied by Dong and Tomchuk (1978). By measuring both the laboratory (T_1) and rotating frame ($T_{1\rho}$) relaxation on methyl deuterated PAA, they found that close to T_{NI} , the slowing down of this optical soft mode (Blinc *et al* 1974) follows the mean field result.

Measurements of T_1 at 10 MHz have been reported on MBBA and OHMBBA at low temperatures in the glassy nematic and supercooled nematic phases by Kumagai *et al*

OHMBBA) which have been interpreted as due to contributions from self-diffusion and end group reorientations respectively.

Proton relaxation in the smectic phases have also attracted a few studies. Blinc *et al* (1975, 1978) studied different phases of TBBA and from the dispersion of T_1 in the 10^5 – 10^8 Hz range, they concluded that in the S_A and S_C phases OF and fast SD make prominent contributions, while in the smectic H and VI phases fast molecular rotations and slow translational self-diffusion determine T_1 . The most complete study on TBBA is again due to Mugele *et al* (1980) who covered the range 100 Hz–44 MHz and found that the relaxation dispersion looks very similar in the S_A and S_C phases and further, that it is analogous to that of a high temperature nematic, *eg*, PAA. Figure 24 shows the relaxation dispersion in the S_C , S_A and N phases. In both S_A and S_C , there is a strong dispersion between 10^3 and 10^5 Hz. This is mainly due to the OF-contribution, perhaps arising from both the fluctuations of the director and of the tilt angle. T_1 is strongly temperature dependent close to the CA and AN transition points. The data over the entire frequency and temperature range could be well fitted with a combination of OF, SD and another mechanism which is assumed to have a Debye-like power spectrum. It may arise either from the highly hindered molecular rotations about the short axis or the fluctuations of the scalar order parameter referred to earlier. The diffusion constant in S_C (at 156°C) is 1.2×10^{-6} cm²/sec, in S_A (at 181°C) 2.7×10^{-6} cm²/sec and in N (at 205°C) 5.4×10^{-6} cm²/sec.

In another study on a few homologues of *p*-alkanoyl-benzylidene-*p'*-aminoazobenzenes, Krüger *et al* (1977) have shown that in the S_B phase the anisotropy of self-diffusion is small and $D_{\perp} > D_{\parallel}$. The diffusion in the smectic A layers ($D_{\perp}$) is liquid-like



whereas $D_{\parallel}$ (from layer to layer) is to be treated as a pseudo-lattice-jump process, and the corresponding activation energy is a few times larger than that for $D_{\perp}$.

Dong (1981) has reported proton spin relaxation measurements at 30 MHz in the N , S_A and reentrant N_R phases exhibited by binary mixtures of two cyano-compounds (see §3.3). In the higher temperature nematic, T_1 decreases with decrease of temperature and has been interpreted to be caused by the SD mechanism (activation energy ≈ 4.6 kcal/mole). In the S_A phase, the same trend continues but with a slightly higher activation energy (≈ 5.6 kcal/mole). However in the N_R phase, T_1 is practically temperature independent and is supposed to be because of the domination of the or mechanism in this phase.

Deuteron relaxation (T_{1Q}) has been studied in a few cases. This technique has the advantage of giving information about intramolecular motion only (Wade 1977; Doane 1979). Emsley *et al* (1976) have determined the relaxation time in the nematic phase of cyano- d_{17} - n -octylbiphenyl between 15 and 35 MHz for the CD_3 deuterons (270 msec) as also the CD_2 deuterons from carbon atoms 4 to 7 (≈ 20 msec) in the chain. They could not explain the results on the basis of director fluctuations alone, and in fact concluded that the dominant contribution comes from the internal motions of the alkyl chain. Rutar *et al* (1978) have studied partially deuterated MBBA between 4–41 MHz and concluded that the benzene ring rotation is the dominant mechanism in this frequency range and that the aniline and benzyldiene rings reorient at different rates around the para-axis.

As in the deuteron case, ^{13}C relaxation also involves only intramolecular processes (Wade 1977; Doane 1979). Figure 25 shows the temperature dependence of relaxation time for the methyl and ring carbons of PAA as determined by Hayamizu and Yamamoto (1977). It is seen that there is no discontinuity in the relaxation times at T_{NI} . These authors have estimated that the rotation about the long molecular axis is $\approx 10^3$ times faster than about the short axis in both the N and I phases. Hutton *et al* (1978) have studied the relaxation of different carbon atoms along the butyl chain of MBBA and found that the flexibility increases as one goes away from the aromatic core. The

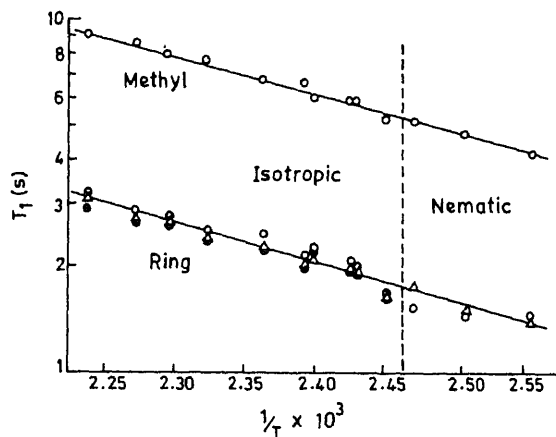


Figure 25. The temperature dependence of the ^{13}C relaxation time in the nematic and isotropic phases of PAA. Open circles, filled circles and triangles in the lower curve represent the

towards T_{NI} , these fluctuations slow down. On the basis of the Landau-de Gennes model (de Gennes 1974; Chandrasekhar 1977), the relaxation rate ($1/T_1$) can be shown to be proportional to $(T - T^*)^{-1/2}$, where T^* is a hypothetical second order transition point slightly below T_{NI} . Many experiments have confirmed this prediction (Cabane and Clark 1970; Ghosh *et al* 1972; Dong *et al* 1974). The relaxation spectrum (from 10^4 – 10^8 Hz) has recently been studied in the isotropic phase of MBBA and EBBA by Reinhart *et al* (1979). At low frequencies T_1 is independent of the frequency but decreases with temperature, while at high frequencies ($> 10^8$ Hz), T_1 is independent of temperature but increases rapidly with increase of frequency. Rollmann *et al* (1979) have studied the relaxation in the isotropic phase of the same compounds using the NMR pulsed field gradient technique. A superposition of the SD mechanism and the fluctuations of the short-range order appears to give a satisfactory fit with the experimental data. They found that $D = 0.9 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ at 50°C for MBBA and $2.5 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ at 89°C for EBBA which agree well with the values obtained from the tracer technique. Further, these results demonstrate the inadequacy of the law $D \propto m^{-1/2}$ where m is the mass of the molecule. It indicates that molecular clusters and not individual molecules may be involved in the transport process.

Ghosh *et al* (1980) have made a detailed analysis of the relaxation spectra of MBBA in its isotropic phase, measured between 4 and 20 MHz. They have argued that the nuclear relaxation rate arising from critical fluctuations (CF) close to T_{NI} should be divided into two parts, one arising from the so-called 'non-local' (N) modes with $q = 0$, and the other from the 'local' (L) critical fluctuations with $q \neq 0$. According to their analysis, T_1 (CFL) follows the Landau-de Gennes theory, but T_1 (CFN) is properly described only by an extended version of that theory. The authors have drawn an analogy between the NI transition and Bose-Einstein condensation.

4.6 Collective modes

We conclude our discussion of molecular dynamics with a brief reference to the problem of collective modes in liquid crystals. This is a major field of study in itself, particularly because it is closely linked with the general problem of phase transitions and pretransition phenomena. A full discussion of this topic is therefore beyond the scope of this article (see de Gennes 1974; Chandrasekhar 1977; Chandrasekhar and Madhusudana 1978). We shall just indicate the methods that are used to investigate the dynamics of these modes.

4.6a Light scattering: As liquid crystals are highly anisotropic media, the orientational fluctuations of the director make the predominant contribution to the light scattering, so much so that the effect of the density fluctuations in the fluid can be ignored altogether. Light scattering is therefore a very important tool for studying the dynamics of collective motions in these phases. The technique involves the use of a laser light beat spectrometer to analyse the scattered radiation; the half-width of the scattered spectrum is a direct measure of the relaxation rate of the orientational fluctuations. A large number of studies have been carried out on the N , S_A and S_C phases and the results have been interpreted in terms of the continuum theory. Light scattering may also be

used to obtain information about the critical slowing down of the par fluctuations near phase transitions, especially transitions which are weakly first (eg, the NI transition) or quasi-second order (eg, the AN or CA transition). These are important for estimating the relevant critical exponents associated with transitions. Here again a number of very careful measurements have been made which have added greatly to our understanding of the nature of these transitions. However, we do not propose to discuss any of these experiments here as an excellent, authoritative article on this very topic (covering also the results of the Kerr effect and other experiments) has been published recently by Schaetzling and Litster (1979).

4.6b Coherent neutron scattering: Coherent inelastic neutron scattering may be used to study collective motions. In this case, the momentum transfer is typically $\approx 10^{-1} \text{ \AA}^{-1}$, which is much larger than with the light scattering technique ($\approx 10^{-3} \text{ \AA}^{-1}$). It is necessary to deuterate the sample fully in order to avoid the incoherent scattering from protons, and very few studies have so far been carried out.

With fully deuterated nematic PAA, Conrad *et al* (1976, 1977a) and Pepy *et al* (1977) have observed broad inelastic peaks which provide evidence of collective phonon excitations in the meV region. Conrad *et al* (1977b, 1980) and Conrad and Mezei (1979) have also studied the AN transition in deuterated CBOA, and observed a line narrowing near T_{AN} due to the slowing down of the smectic order fluctuations. Furthermore, using neutron-spin-echo spectroscopy they have estimated a characteristic decay time of $\approx 10^{-8} \text{ sec}$ for the smectic fluctuations.

Benattar *et al* (1979) have investigated the lattice dynamics of three 3D phases of deuterated TBBA—the room temperature crystal, S_B and S_E (or according to the revised notation of Gray (1981) and Demus *et al* (1980), S_C and S_H) phases—monodomain samples. They confined their experiments to the a^*c^* plane and found that both longitudinal and transverse phonons propagate in all three phases. However, while the longitudinal mode is practically unaltered in the three phases, the frequency of the transverse mode as well as the width of the transverse mode along c^* are larger in the smectic phases.

4.6c Ultrasonic relaxation: Though the first ultrasonic studies of the NI transition were carried out long ago, accurate relaxation measurements on magnetically aligned samples have been made only recently. The experiments up to 1978 have been reviewed by Candau and Letcher (1978) and we summarize only some of the more recent work on the NI and AN transitions.

Close to these phase transition points, fluctuations of the order parameter couple strongly to the ultrasonic relaxation. Imura and Okano (1973) and Matsushita (1978) developed the theory for this process by assuming that the temperature oscillations accompanying the sound wave get coupled to the order parameter fluctuations. As the transition is approached, the fluctuations grow larger and become slower and cannot follow the temperature oscillations. This phase lag produces a frequency dependent heat capacity which results in an additional contribution to the ultrasonic relaxation. While this is the only contribution in the isotropic phase, on the nematic side the order parameter fluctuations directly couple to the ultrasonic waves through pressure and temperature variations (the Landau-Khalatnikov process).

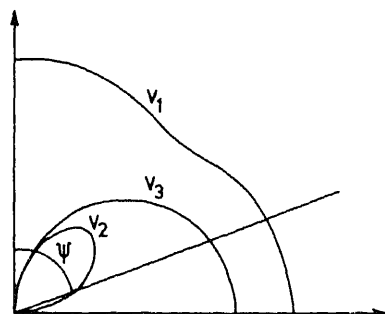
The fluctuation contribution leads to the result that $\alpha/f^2 \approx |T - T^*|^{-1.5}$ where α is the attenuation coefficient and f the frequency. This result has been confirmed for the isotropic phase of PAA (Thiriet and Martinoty 1979) and 5CB (Nagai *et al* 1979).

director for temperatures below $(T_{NI}-1)K$, the critical part of the attenuation coefficient in the N phase of PAA was found to vary as $(T_1-T)^{-1}$, where T_1 is a temperature close to T_{NI} (Thiriet and Martinoty 1979). This temperature dependence clearly indicates that the relaxation of the order parameter (and *not* that of its fluctuations) makes the dominant contribution in this phase. One may expect however that fluctuations do make an important contribution very close to T_{NI} , but measurements could not be carried out in this range because of experimental difficulties.

In the case of compounds like MBBA (Castro *et al* 1978) and 5CB (Nagai *et al* 1976) with relatively long end chains, the relaxation due to rotational isomerism of the chains has to be properly accounted for before the critical part of the relaxation can be analysed. Recent results on MBBA (Castro *et al* 1978) tend to confirm the importance of the Landau-Khalatnikov mechanism in the N phase.

Ultrasonic relaxation studies near the AN transition have been made on CBOOA in both low frequency (0.6–25 MHz) (Kiry and Martinoty 1978) and high frequency (200–1000 MHz) (Bacri 1975) regions. The critical increase in the absorption is apparent on the nematic side as the frequency is lowered. Here both the divergence of some viscosity coefficients and the frequency dependent heat capacity discussed earlier contribute to the relaxation. In the S_A phase, the Landau-Khalatnikov process and the intramolecular (chain reorientation) processes make the analysis somewhat difficult. Much more pronounced attenuation is observed near the AN transition of TBBA (Bhattacharya *et al* 1978). Martinoty (1979) has argued that this is connected with the large value of the excess heat capacity due to fluctuations in TBBA—larger by about an order of magnitude than in the case of CBOOA.

4.6d Brillouin scattering: (Schaetzing and Litster 1979). In the S_A phase there are two propagating acoustic modes for any arbitrary direction of the wavevector. One is the usual longitudinal wave whose velocity is practically independent of the direction of propagation. The other is a transverse wave associated with changes in the layer spacing at nearly constant density and is referred to as *second sound* (de Gennes 1974; Chandrasekhar 1977). The velocity of this mode is strongly orientation dependent, becoming zero along as well as perpendicular to the layers. Direct evidence of these two branches has been obtained by Brillouin scattering studies (Bradberry and Vaughan 1977; Ricard and Prost 1979; Liao *et al* 1973; Conrad *et al* 1977b). The velocity of



second sound is expected to show critical behaviour near the AN transition, but the experimental data are not quite conclusive on this point.

In the case of columnar liquid crystals, continuum theory shows that there can be three propagating modes (Kats 1978; Prost and Clark 1980). The expected angular dependence of their velocities is shown in figure 26 (Prost and Clark 1980). Two of the modes (with velocities V_1 and V_2) are analogous to the first and second sounds of S_A . There is now another transverse mode which for propagation along the basal plane is polarized in the plane itself and since the two-dimensional lattice can sustain a shear its velocity V_3 does not vanish. For propagation along the columns, this wave becomes the highly damped undulation mode with zero velocity. Consequently, depending on the orientation, there should be one, two or three pairs of Brillouin components, but no experiments have yet been carried out.

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Molecular motion in plastic crystals

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1. Introduction

Many crystalline substances pass through an intermediate crystalline state before melting and the entropy of fusion is generally lower than that of the transition from the ordered crystalline state to the intermediate phase. The intermediate phase, commonly referred to as the plastic state, has high symmetry (generally cubic), and the molecules are orientationally disordered in this phase (Aston 1963; Sherwood 1979). Due to this disorder as well as the large amplitudes of molecular librations, X-ray diffraction studies provide limited structural information on the plastic crystalline state. Much knowledge has however been gained about the molecular motions in plastic crystals through spectroscopic studies. In particular, NMR spectroscopy, neutron scattering as well as Raman and infrared spectroscopy have been most useful.

It was originally believed that the plastic state was exhibited only by spherical (globular) molecules. Plastic states of many molecules, some of relatively low symmetry, have been established (see table 1). In this article, we shall briefly describe the

Table 1. Thermodynamic data on organic plastic crystals^a.

Compound	T_{cp} (K)	T_{pl} (K)	ΔS_{cp} J/mol/K	ΔS_{pl} J/mol/K	ΔH_{cp} kJ/mol	ΔH_{pl} kJ/mol
1. 2,3-Dimethylbutane	136	145	47.7	5.5	6.5	0.8
2. Carbon tetrachloride	216.5, 228	242	21.8, 3.2	7.0	4.7, 0.75	1.7
3. Cyclohexanone	222	240.5	34.5	4.7	7.6	1.1
4. <i>t</i> -Butylbromide	208.5, 231	256.0	27.3, 4.6	7.5	5.7, 1.0	2.0
5. <i>t</i> -Butylchloride	183, 219.5	248.0	9.3 26.4	8.0	1.7, 5.8	2.0
6. Cyclobutane	145.7	182	39.2	5.9	5.7	1.1
7. Carbon tetrabromide	320	363	20.8	10.8	6.6	4.0
8. 2,2-Dimethylbutane	126.8	174	42.5	3.3	5.4	0.6
9. Cyclopentane	122	180	39.8	3.3	4.9	0.6
10. Succinonitrile	236	326	11	4.6	2.6	1.5
11. Cyclohexane	186	278	36	9.0	6.7	2.5
12. Neopentane	140	257	18.5	12.6	2.6	3.2
13. <i>t</i> -Butylmercaptan	152	274	26.8	9.0	4.0	2.5

nature of molecular motion in plastic crystals and the spectroscopic techniques available to study the motion. We shall then examine typical results obtained in recent years employing NMR, neutron scattering, infrared and Raman spectroscopy, ESR spectroscopy as well as computer simulation.

2. Models for reorientational motion

Existence of a high degree of orientational freedom is the most characteristic feature of the plastic crystalline state. We can visualize three types of rotational motions in crystals: free rotation, rotational diffusion and jump reorientation. Free rotation is possible when interactions are weak—this situation would not be applicable to plastic crystals. In classical rotational diffusion (proposed by Debye to explain dielectric relaxation in liquids), orientational motion of molecules is expected to follow a diffusion equation described by an Einstein type relation. This type of diffusion is not known to be applicable to plastic crystals. What would be more appropriate to consider in the case of plastic crystals is collision-interrupted molecular rotation.

The rotational diffusion model was generalized by Gordon (1966) to include molecular reorientation in angular steps of fairly large size. According to this model, the molecules are supposed to freely rotate during the intervals between collisions. Two limiting cases have been discussed by Gordon, both of which involve angular diffusion steps (of arbitrary size). These are commonly known as the *J*-diffusion and the *M*-diffusion models. In the former, the direction as well as the magnitude of the angular momentum vector of the molecule follow a Boltzmann distribution due to collisions. In the *M*-diffusion model, the orientation of the angular momentum vector is randomized, but the magnitude is unchanged. In Gordon's model applied to linear molecules, the general diffusion equation follows classical mechanics at short times. At longer times, the rotational frequency is unchanged in successive steps in the *M*-diffusion model while it follows the Boltzmann distribution in the *J*-diffusion model.

Another model (Hill 1963; Wyllie 1971) has been proposed wherein the molecules exhibit librations (perturbed angular oscillations), having been trapped in potential wells. Fluctuations in orientation of neighbouring molecules result in a change in the shape of the potential well and consequently give rise to angular motion of molecules with large amplitudes. It is possible that diffusion of the potential well on the surface of a sphere gives rise to reorientational motion of molecules. If the potential surface is related to the crystal space group, molecular reorientation will be associated with damped librations (Guthrie and McCullough 1961). Rotations of the crystal space group will give rise to allowed potential wells.

No single model can exactly describe molecular reorientation in plastic crystals. Models which include features of the different models described above have been considered. For example, diffusion motion interrupted by orientation jumps has been considered to be responsible for molecular reorientation. This model has been somewhat successful in the case of cyclohexane and neopentane (Lechner 1972; De Graaf 1969; De Graaf and Schieskinski 1970). What is not yet completely clear is whether the reorientational motion is cooperative. There appears to be some evidence for coupling between the reorientational motion and the motions of neighbouring molecules. It would appear that there is scope for comparative experimental studies employing complementary techniques which are sensitive to autocorrelation and

3. Methods of studying molecular motion

The nature of rotational motion responsible for orientational disorder in plastic crystals is not completely understood and a variety of experimental techniques have been employed to investigate this interesting problem. There can be coupling between rotation and translation motion, the simplest form of the latter being self-diffusion. The diffusion constant D is given by the Einstein relation,

$$D = \langle r^2 \rangle / 6\tau,$$

where $\langle r^2 \rangle$ is the mean-square-jump distance and τ is the mean time between successive jumps of a molecule at a lattice site. The diffusion constant depends on the magnitude of molecular velocity as well as the persistence velocity. Both radioactive tracer and NMR methods have been employed to measure the coefficients of self-diffusion in plastic crystals. In many cases, the two methods yield similar results since they refer to a similar process on the time scales of the velocity correlation function.

NMR spectroscopy provides spin-lattice (T_1) and spin-spin (T_2) relaxation times. Making appropriate assumptions with regard to the magnetic interactions responsible for the relaxation process, these relaxation times can be related to molecular motion. Since nuclear spin relaxation results from all processes which cause a fluctuation in the magnetic field at the nucleus, the correlation function will generally correspond to more than one kind of motion involving all possible interactions. The equations for the relaxation times are generally of the form,

$$1/T = C\tau/(1 + \omega^2\tau^2),$$

where the constant of proportionality, C , as well as τ are determined by the nature of the nucleus and the different interactions. If the relaxation process is essentially due to dipolar interactions, then NMR spectroscopy gives information on rotational diffusion. If nuclear quadrupole relaxation is dominant, then we obtain information on molecular reorientation.

Thermal or low energy neutron scattering experiments have been most valuable in throwing light on molecular motion in plastic crystals. These experiments measure changes in the centre of mass of a molecule. Diffusion constants obtained from neutron experiments differ widely from those obtained from tracer experiments since neutron scattering is mainly determined by rotational diffusion. The scattering function has the form,

$$S(\mathbf{Q}, \omega) = \iint G(\mathbf{R}, t) \exp(i\mathbf{Q}\mathbf{r} - i\omega t) d\mathbf{Q} \cdot d\omega$$

where $G(\mathbf{R}, t)$ is the rotational correlation function for a scattering centre, $\mathbf{Q}$, the scattering vector, ω , the angular frequency and $\mathbf{R}$, the equilibrium position vector. The inelastic part of the scattering provides information on the rotational motion while the elastic part is related to the translational motion. If the reorientational motion is

$\langle \mu(t_0) \cdot \mu(t_0 + t) \rangle$, for the motion about a specific molecular axis with respect to the principal rotation axes and the direction of vibration. Rayleigh scattering as well as Raman scattering are most useful in the study of molecular orientational processes. With the aid of isotropic and anisotropic Raman scattering measurements, orientational processes can be delineated from other mechanisms which cause line broadening. Analysis of infrared and Raman bandshapes provides information on the short and long term behaviour of the correlation function.

Correlation times and activation energy parameters obtained from different techniques may or may not agree with one another. Comparison of these data enables one to check the applicability of the model employed and examine whether any particular basic molecular process is reflected by the measurement or whether the method of analysis employed is correct. In order to properly characterize rotational motion in plastic crystals it may indeed be necessary to compare correlation times obtained by several methods. Thus, values from NMR spectroscopy and Rayleigh scattering enable us to distinguish uncorrelated and correlated rotations. Molecular disorder is not reflected in NMR measurements; to this end, diffraction studies would be essential.

4. NMR studies

NMR spectra of molecular crystals are generally broad due to dipolar interactions between the spins. It is most useful to relate the frequency domain spectrum to the properties of the spin system by employing the van Vleck method of moments. The n th moment of the frequency domain spectrum is given by,

$$M(n) = \frac{\int_0^\infty (\omega - \omega_0)^n F(\omega) d\omega}{\int_0^\infty F(\omega) d\omega}$$

where $F(\omega)$ is the frequency domain spectrum and ω_0 is the centre of the resonance line. The second moment, $M(2)$ has been found to be of great value since it is directly related to the geometric arrangement of spins. Experimental second moments in the presence of thermal motion is given by,

$$M(2) = \frac{3\mu^2 \hbar^2}{16\pi^2 n} \gamma^4 I(I+1) \sum_{i,j} \left[\frac{1 - 3 \cos^2 \theta_{ij}}{r_{ij}^3} \right]$$

Here, γ is the gyromagnetic ratio, I , the spin quantum number, θ_{ij} , the orientation of the vector $\mathbf{r}_{ij}$ from spin i to j with respect to the direction of the applied magnetic field and the summation is for each of n spins i over all its neighbours j . The term in square brackets is an average over the motion as well as over the various orientations in powder samples. The above equation is applicable when $M^{1/2}(2) \tau \ll 1$ where τ is the correlation time for the motion of the spin-spin vector. Boden (1979) has reviewed applications of NMR spectroscopy to plastic crystals in detail.

The experimental second moment of a solid containing molecules which undergo thermally activated reorientation varies with temperature as shown in figure 1. The abrupt drop in $M(2)$ is due to motional narrowing of the resonance line and under these

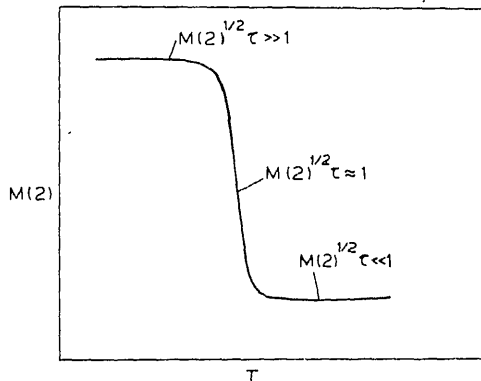


Figure 1. Temperature variation of the second moment $M(2)$ in a solid due to reorientational motion of molecules. When $M(2)^{1/2}\tau \gg 1$, we have the rigid lattice value; when $M(2)^{1/2}\tau \ll 1$, we have the motionally averaged value; motional narrowing occurs at $M(2)^{1/2}\tau \approx 1$.

$M(2)$ and under these conditions $M^{1/2}(2)\tau \approx 1$. We thus see that the mechanism of the reorientation (rotational) process giving rise to motional narrowing can be readily found from $M(2)$ measurements. In the case of protons, motional narrowing occurs when τ is of the order of 10^{-5} sec. Values of τ can be roughly estimated from experimental $M(2)$ data in the transition region from the expression,

$$M(2) = M(2)_{\text{ave}} + \frac{2}{\pi} (M(2)_r - M(2)_{\text{ave}}) \tan^{-1} (M^{1/2}(2)_r \tau)$$

where $M(2)_r$ and $M(2)_{\text{ave}}$ correspond to the rigid lattice and motionally averaged values (Gutowsky and Pake 1950; Andrew and Lipofsky 1972). $M(2)$ generally shows abrupt changes in structural phase transitions and the change in $M(2)$ depends on molecular shape (symmetry) and packing. Thus, in cyclohexane (Andrew and Eades 1953), we see a decrease in $M(2)$ at T_{cp} before a motionally averaged value is reached (figure 2). In adamantane, there is a large drop in $M(2)$ around 145 K but almost no change at T_{cp} . In camphor, on the other hand, there is almost no motional averaging below T_{cp} . In many instances, the nature of change in $M(2)$ reflects the occurrence of extensive disordering prior to the crystal-plastic transition and $M(2)$ changes continuously from the crystal to the plastic state, the large drop in $M(2)$ being well before T_{cp} . Boden (1979) cites several examples in his review article.

The behaviour of $M(2)$ generally appears to be independent of the shape of the molecule in the plastic state and is generally of the order of $1G^2$. The rotationally averaged value of $M(2)$ is related to the spin-spin relaxation time, T_2 , and linewidth at half-maximum, $\Delta\omega_{1/2}$, as follows:

$$M(2)\tau = \frac{1}{T_2} = 1/2(\Delta\omega_{1/2}).$$

Linewidth measurements give useful information on molecular diffusion in plastic

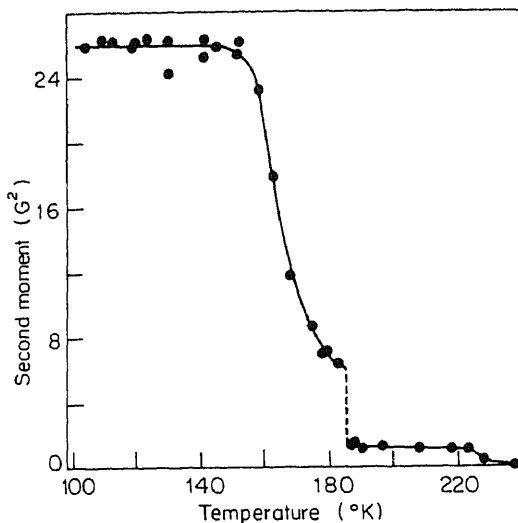


Figure 2. Temperature variation of the second moment of (the proton NMR spectra) cyclohexane (after Andrew and Eades 1953).

intramolecular dipolar interaction as well as nuclear electric quadrupole and anisotropic chemical shielding tensors to average to zero. The intermolecular dipolar interaction, is however, averaged only partially by the rotation motion and therefore affects the shape of the spectrum. Since intermolecular interactions are averaged out by the translational motion at the melting point, NMR linewidths can be used to obtain estimates of the diffusion rate. Spin relaxation measurements give much better estimates of this important property.

Both rotational and translational diffusion of molecules can be investigated effectively by spin relaxation measurements. The various quantities measured experimentally are, the spin-lattice relaxation times in laboratory and rotating frames, T_1 and T_{1r} , and the spin-spin relaxation time, T_2 . Relations between these relaxation times and the reorientational correlation (autocorrelation) time, τ_2 , are as follows:

$$\frac{1}{T_1} = \frac{2}{3} M(2) \frac{\tau_2}{1 + \omega_0^2 \tau_2^2} + \frac{4\tau_2}{1 + 4\omega_0^2 \tau_2^2},$$

$$\frac{1}{T_{1r}} = \frac{1}{6} M(2) \frac{4\tau_2}{1 + 4\omega_0^2 \tau_2^2} + \frac{10\tau_2}{1 + \omega_0^2 \tau_2^2} + \frac{6\tau_2}{1 + 4\omega_1^2 \tau_1^2},$$

$$\frac{1}{T_2} = \frac{1}{6} M(2) 6\tau_2 + \frac{10\tau_2}{1 + \omega_0^2 \tau_2^2} + \frac{4\tau_2}{1 + 4\omega_0^2 \tau_2^2},$$

where $\omega_0 = \gamma B_0$ and $\omega_1 = \gamma B_1$ where B_0 and B_1 are given by the applied static magnetic field and the field rotating perpendicularly about B_0 respectively. The correlation time τ_2 reflects the average life time of molecules in an equilibrium orientation and $M(2)$ is

molecular reorientation is fast as at high temperatures ($\omega_0\tau_2 \ll 1$) or in the plastic phase,

$$1/T_1 = C_1\tau_2.$$

At low temperatures ($\omega_0\tau_2 \gg 1$),

$$1/T_1 = C_2/\omega_0^2\tau_2.$$

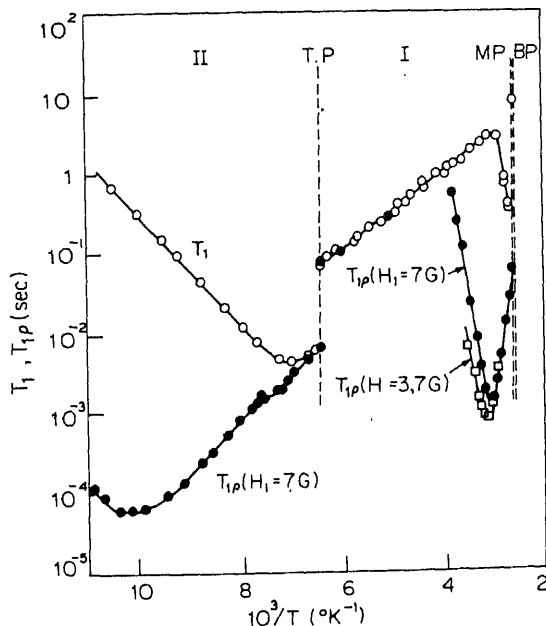
Measurements of T_1 as a function of temperature and frequency enable us to understand the nature of molecular motion and to determine the correlation time. In figure 3 we show the temperature variation of the proton relaxation times in hexamethylethane in the ordered crystalline and the plastic crystalline phases. In the low-temperature ordered crystalline phase, the reorientation of the molecule about the 3-fold axis is reflected in the measurements. The slopes of the plots of T_1 and T_{1r} are the same and both show minima as expected from theory; T_1 in the plastic phase clearly reflects the rapid reorientation of molecules ($\omega_0\tau_2 \ll 1$). Near the melting point, T_1 is affected by translational motion as well.

Measurements of T_{1r} can detect motion of molecules with frequencies of the order of ω_1 . The dipolar relaxation time T_{1d} which measures the rate at which the dipolar energy relaxes to the lattice is given by

$$1/T_{1d} = 2/T_{1r} = 2/T_1,$$

when $\omega_0\tau \ll 1$ when the motion of spins is not correlated; if the motion is correlated, we have 3 instead of 2 in the numerators of the above equations.

In the case of plastic phases ($\omega_0\tau \ll 1$), T_1 measurements (note that $(1/T_1) = C_1\tau_2$



where C_1 is a constant) directly give τ_2 or the area under the rotational correlation function

$$\tau_2 = \int_0^{\infty} G(\tau) d\tau$$

subject to $\lim_{\tau \rightarrow \infty} G(\tau) = 0$. Such measurements have been carried out on several molecules in the plastic state. In table 2, we list typical values of activation energies for molecular reorientation in the plastic phases of a few compounds obtained from the slopes of the Arrhenius plots of T_1 . In some cases, non-Arrhenius behaviour has been found, with the $\log T_1$ vs $1/T$ plots showing more than one linear region. A continuous decrease in activation energy with temperature has also been noticed (suggesting progressive increase in orientational disorder.)

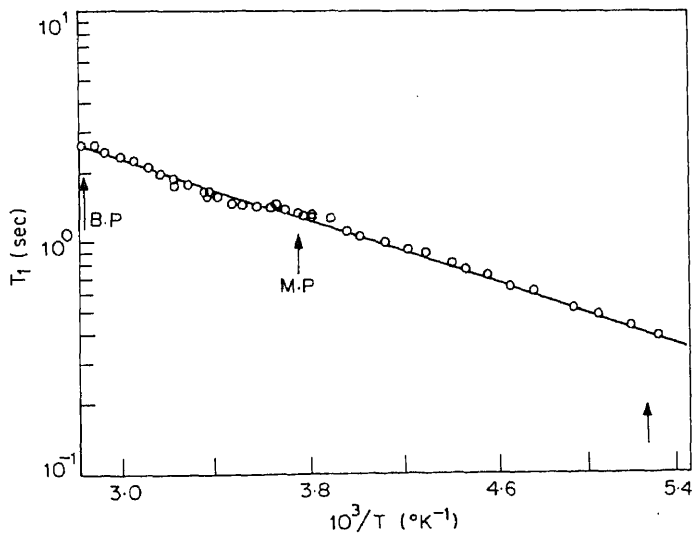
A number of systems do not show any discontinuity in T_1 across the plastic-liquid transition as illustrated by the case of C_6D_{12} in figure 4. This behaviour can be taken to

Table 2. Energies of activation for molecular motion in some organic plastic crystals obtained from NMR spectroscopy^a.

	Structure	ΔS_f^b	E_a (kJ mol ⁻¹)
Adamantane	FCC	20.8	12.9
Neopentane	FCC	12.6	4.2
Cyclohexane	FCC	9.0	6.4
Pivalic acid	FCC	6.3	36
Hexamethylethane	BCC	20.0	9.2
DL-Camphene	BCC	9.5	4.9–6.5 ^c

^a Data taken from Boden (1979); ^b Entropy of fusion in J mol⁻¹ K⁻¹;

^c Depending on the temperature in the range 175–323 K.



imply that the collision process controlling the molecular reorientation remains the same in both the plastic and liquid phases. Discontinuous changes have also been noticed in a few systems implying that the molecular field changes across the plastic-liquid transition. The fact that τ at the plastic-liquid transition is nearly equal to or about twice the value at the melting point shows that nearly half the nearest neighbour molecules are rotating at the same time, possibly in a correlated manner.

Translational motion of spins in the plastic crystalline state has been interpreted on the basis of a model involving random-walk of a discrete isotropic crystal lattice (Torrey 1954; Resing and Torrey 1963) or a monovacancy diffusion mechanism (Wolf 1975). Experimentally, it has been found that the measurements are consistent with Torrey's model as well as radiotracer studies in the case of solids with high entropies of fusion. No such agreement is found in the case of solids with low entropies of fusion. Typical results from NMR and radiotracer measurements are shown in table 3. Self-diffusion parameters obtained from spin relaxation measurements do not appear to be very sensitive to the microscopic model employed. The main application of NMR spectroscopy in the study of the plastic crystalline state has been in the determination of the mean time interval between translational jumps.

5. Neutron scattering studies

The equation for incoherent rotational scattering of neutrons can be written as,

$$S_r(\mathbf{Q}, \omega) = A_{ei}(\mathbf{Q}) \delta(\omega) + S_{qe}(\mathbf{Q}, \omega)$$

where $S_{qe}(\mathbf{Q}, \omega)$ is the quasielastic scattering and $A_{ei}(\mathbf{Q})$ is the elastic incoherent structure factor which provides a measure of the time-averaged spatial distribution of the proton and therefore about the nature of the rotational motion of molecules. The rotational correlation time determines the width of $S_{qe}(\mathbf{Q}, \omega)$. If we can experimentally determine $A_{ei}(\mathbf{Q})$ from neutron scattering experiments, we can obtain valuable information about the time scale as well as the kind of rotational motion in plastic crystals. Correlation times shorter than $\sim 10^{-9}$ sec are generally studied with the available resolution of instruments today.

Study of the rotation of near-spherical molecules by neutron scattering enables us to determine how far the rotation is isotropic. Typical of such molecules studied are

Table 3. Data for self-diffusion in plastic crystals^a.

	Structure	ΔS_f^b	NMR ^c $\tau(s)$	Radiotracer ^c $\tau(s)$
Adamantane	FCC	20.8	1.6×10^{-21} (153)	4.6×10^{-20} (139)
Neopentane	FCC	12.6	1.2×10^{-13} (33)	—
Cyclohexane	FCC	9.0	9.1×10^{-15} (42)	6.3×10^{-25} (92)
Pivalic acid	FCC	6.3	2.7×10^{-17} (63)	1.3×10^{-22} (91)
Hexamethylethane	BCC	20.0	2.5×10^{-19} (82)	3.2×10^{-20} (86)
DL-Camphene	BCC	9.5	4.6×10^{-17} (57)	3.8×10^{-24} (96)

methane, neopentane, adamantane and cyclohexane. Leadbetter and Lechner (1979) have reviewed results on these and other systems at length. In the plastic state of adamantane, rotational jump models seem to be applicable rather than an isotropic rotation model. In the case of succinonitrile, two correlation times have been considered, one due to *gauche-trans* isomerization and another due to the rotation of the *trans* isomer. Both these correlation times have been estimated from neutron scattering experiments.

6. Raman and infrared spectroscopic studies

The experimental dipole correlation function is obtained from the observed spectral density as follows (Gordon 1965):

$$\phi(t) = \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle = \int_{\text{band}} \hat{I}(\omega) \exp - (i\omega t) \times d\omega$$

where $\hat{I}(\omega) = I(\omega) / \int_{\text{band}} I(\omega) d\omega$. Normally, only the real part of $\phi(t)$ is calculated and we have,

$$\phi(t) = \int_{\text{band}} \hat{I}(\omega) \cos [(\omega - \omega_0)t] d\omega$$

where ω_0 is the band centre. Dipole correlation functions obtained in this manner from bandshapes are rotation-vibration correlation functions. Vibrational relaxation contributes significantly to vibrational band shapes (Nafe and Peticolas 1972) and one has to be careful in extracting information on molecular reorientation from such data. For Raman active totally symmetric vibrations of a linear or a symmetric top molecule (Gordon 1965),

$$\phi(t) = \langle P_2[\mathbf{u}_z(0) \cdot \mathbf{u}_z(t)] \rangle.$$

For a tetrahedral molecule,

$$\phi(t) = \langle P_2[\mathbf{u}_2(0) \cdot \mathbf{u}_2(t)] \rangle,$$

where $\mathbf{u}_2$ is the unit vector along a two-fold axis. Vibration relaxation has to be included in analysing Raman bandshapes as well.

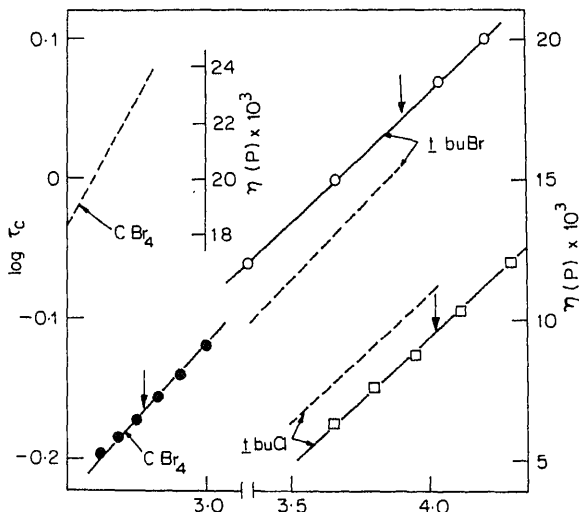
It is generally difficult to locate infrared bands of plastic crystals which are suitable for the analysis of bandshapes. This is due to the proximity of overtones, hot bands, overlapping fundamentals and combination tones. Furthermore, vibrational relaxation contributes prominently to infrared bandshapes. In Raman scattering, however, it is often possible to delineate reorientational relaxation from other band broadening mechanisms by carrying out both anisotropic and isotropic measurements. By comparing reorientational correlation times obtained from Raman studies with those from NMR studies, one can obtain valuable information on the anisotropy of molecular reorientations in plastic crystals. Applications of Raman and infrared spectroscopy to the study of plastic crystalline state of molecules have been reviewed by Bailey (1979) and we shall only briefly look at some of the results.

Raman studies of CCl_4 by Bartoli and Litovitz (1972) gave a orientational correlation time of 1.8×10^{-12} sec. Furthermore, $\tau(\text{Raman})$ showed no discontinuity

et al 1983). Ganguly *et al* (1983) find reorientational correlation times in the range $1.5\text{--}2.3 \times 10^{-12}$ sec in the plastic phases of *t*-butyl chloride, *t*-butyl bromide and succinonitrile. Correlation times obtained from Raman bandshapes of CCl_4 by Sundar and McClung (1973) could be fitted into the *J*-diffusion model, the τ_j from this model showing fair agreement with NMR results.

Ganguly *et al* (1981) find no discontinuity in τ (determined from infrared band shapes) across the plastic-liquid transitions of many systems (figure 5) indicating the presence of appreciable rotational motion in the plastic phase. It appears that rotational motion is not through translational jumps. In the case of neopentane, both IR and Raman spectroscopy give activation energies of 4 kJ mol^{-1} (Ganguly *et al* 1981); the values from NMR and neutron scattering measurements are also close to this value. Both *t*-butyl chloride and *t*-butyl bromide are found to have activation energies of $\sim 3.5 \text{ kJ mol}^{-1}$ from infrared studies (Ganguly *et al* 1981); Raman and NMR values for *t*-butyl chloride are both around 3 kJ mol^{-1} . Raman studies of Ganguly *et al* (1983) give a value close to 3 kJ mol^{-1} for E_a in *t*-butyl bromide. IR studies give an E_a of 4.7 kJ mol^{-1} in the case of cyclohexane (Ganguly *et al* 1981) and the NMR value is 6.4 kJ mol^{-1} .

In the case of neopentane, Livingston *et al* (1973) have compared the infrared and Raman correlation functions with the functions calculated from the *J* and *M* diffusion models (figure 6). Experimental correlation functions are found to be in-between those predicted by the two diffusion models. Succinonitrile is an unusual non-globular molecule which occurs in the plastic state. The plastic state contains both *gauche* and *trans* forms, while the ordered crystalline phase contains only the former. Infrared studies of Ganguly *et al* (1981) give a very low value of E_a compared to the NMR value (25 kJ mol^{-1}); recent Raman studies (Ganguly *et al* 1983) however give a value of 12 kJ mol^{-1} . Camphor also appears to exhibit anomalous reorientational behaviour;



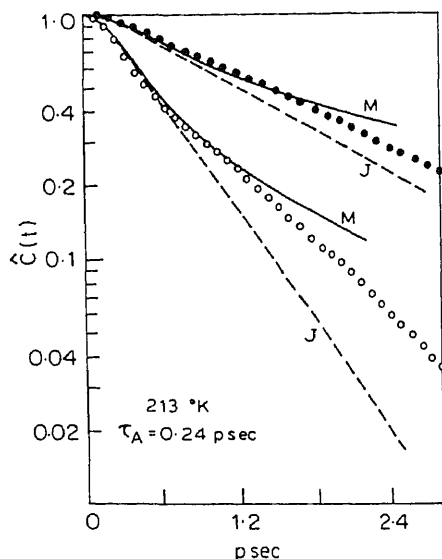


Figure 6. Raman (○) and IR (●) correlation functions for the plastic phase of neopentane (942 cm^{-1} band at 213 K) compared with the function predicted from M and J diffusion models. (after Livingston *et al* 1973).

Ganguly *et al* find an E_a of $\sim 7\text{ kJ mol}^{-1}$ from IR band shape analysis while NMR gives a value of 11 kJ mol^{-1} .

Far-infrared absorption of plastic crystals provides useful information on libration motions of molecules as influenced by collisions with neighbouring molecules. This region includes the Debye plateau ($10\text{--}100\text{ cm}^{-1}$ region) due to the diffusion of dipoles, absorption above the plateau due to torsional oscillations of dipoles and also absorption due to dipoles induced by neighbouring molecules. Larkin (1973) and Larkin and Evans (1974) have examined this region of the infrared spectrum in plastic crystals and liquids.

Ganguly *et al* (1981) have carried out studies of solute molecules (upto a mole fraction of 0.2) dissolved in cyclohexane or carbon tetrachloride. Infrared correlation functions of *t*-butyl bromide in CCl_4 and cyclohexane solutions in the plastic state are compared with the correlation function for the pure substance (in the plastic state) in figure 7. The correlation function of pure cyclohexane is compared with the function found in CCl_4 solution in the same figure. In the case of *t*-butyl chloride (or *t*-butyl bromide) dissolved in cyclohexane, we find that the half-width of the C–Cl (or C–Br) stretching band decreases (or τ_c increases) significantly with the increase in mole fraction of the halide in the plastic phase (figure 8). This suggests that there is an increase in rotation rate, with respect to the pure material, of these solute molecules in the plastic phase when present in small concentration in the host matrix of cyclohexane. In the liquid state, however, τ_c decreases with increase in halide concentration implying that there is a decrease in the rotation rate of the halide (in the liquid state) when it is surrounded by cyclohexane solvent molecules. Camphor shows results similar to *t*-

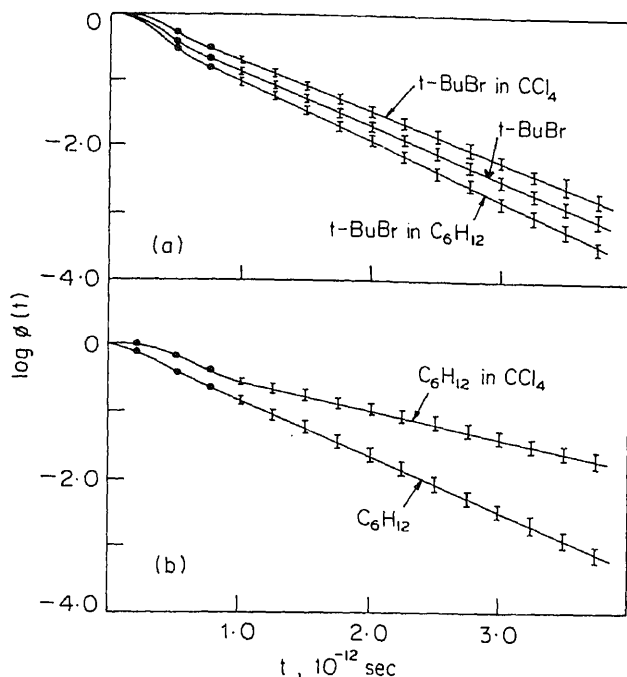


Figure 7. (a) Infrared correlation functions of pure *t*-butyl bromide and in CCl_4 and C_6H_{12} solutions, all in the plastic state at 233 K (mole fraction of *t*-butyl bromide = 0.05). (b) Correlation function of cyclohexane in the pure state and in CCl_4 solution, both in the plastic state at 233 K (mole fraction of cyclohexane = 0.05) (after Ganguly *et al* 1981).

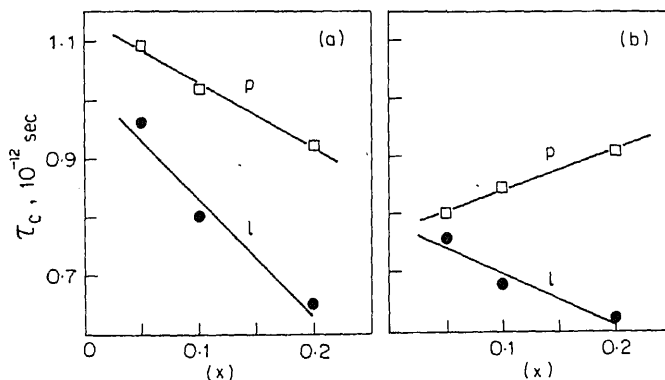


Figure 8. Plots of IR τ_c values against the mole fraction of *t*-butyl bromide in (a) CCl_4 and (b) C_6H_{12} at 233 K. The 'p' and 'l' refer to the plastic and liquid phases, respectively.

in cyclohexane and CCl_4 solutions (figure 7). Correlation functions of cyclohexane in figure 7 show that there is a decrease in rotation when it is surrounded by CCl_4 solvent molecules. It is also interesting that unlike in cyclohexane, the concentration dependence of τ_c in CCl_4 solvent is the same both in the liquid and plastic phases. The above variations in τ_c could at least partly be due to vibrational relaxation in solutions which in turn gives rise to vibrational dephasing or inhomogeneous broadening due to frequency fluctuations. Whatever be the exact origin, the trends in τ_c of solute molecules in the plastic and the liquid states are quite interesting and may provide a means of understanding the effect of solute-solvent interactions on vibrational bands. The difference in the concentration-dependence of τ_c of the solute molecule in the plastic state in cyclohexane and CCl_4 solvents may be related to the ΔS_{cp} values of the solvent relative to that of the solute molecule. In the case of cyclohexane solvent, both the *t*-butyl halides have lower ΔS_{cp} values; the ΔS_{cp} values of both *t*-butyl bromide and cyclohexane are higher than the ΔS_{cp} of CCl_4 .

7. ESR studies

Ganguly *et al* (1981) have recently obtained ESR spectra of the spin-probe TEMPO in the plastic and liquid phases of cyclohexane, CCl_4 and *t*-butyl chloride; the spectra were damped out in the crystalline phase. We have evaluated the correlation times for the tumbling, τ_t , of these molecules in both the plastic and liquid states by employing McConnell's method (Stone *et al* 1965) and find them to be continuous through the plastic-liquid transition (figure 9), just as the τ values from IR and Raman spectroscopy. The activation energies calculated from the $\log \tau_t - 1/T$ plots in figure 9 are 3.5, 4.0 and 11 kJ mol⁻¹ for CCl_4 , *t*-butyl chloride and cyclohexane respectively. These activation energies vary in the same direction as the E_a values from IR studies and the ΔH values of the plastic-crystal transitions (4.7, 5.8 and 6.7 kJ mol⁻¹ respectively for CCl_4 , *t*-butyl chloride and cyclohexane). Ganguly *et al* (1981) point out that in the systems studied by them, the E_a values from IR correlation times vary in the same direction as the ΔH_{cp} .

8. Thermodynamics of organic plastic crystals

One of the important characteristics of the plastic state is that the entropy change of the crystal to plastic transition, ΔS_{cp} , is generally much larger than the entropy change of the transition from the plastic to the liquid state, ΔS_{pl} . It is instructive to examine possible systematics in the thermodynamics of the crystal-plastic and plastic-liquid phase transitions and the range of stability of the plastic phase in a few systems. In table 1, thermodynamic data on the transitions of a few chosen systems are listed. It has been found by Ganguly *et al* (1981) that the ΔH of the crystal-plastic transition, ΔH_{cp} , generally decreases as the range of stability, ΔT_{pl} ($\Delta T_{pl} = T_{pl} - T_{cp}$) increases. The ΔH of the plastic-liquid transition, ΔH_{pl} , on the other hand, increases as ΔT_{pl} increases (figure 10). Similar trends are also shown by ΔS_{cp} and ΔS_{pl} of the transitions. The ΔS_{cp} and ΔS_{pl} values show similar trends with $\Delta T_{pl}/T_{pl}$ where T_{pl} is the melting point. The

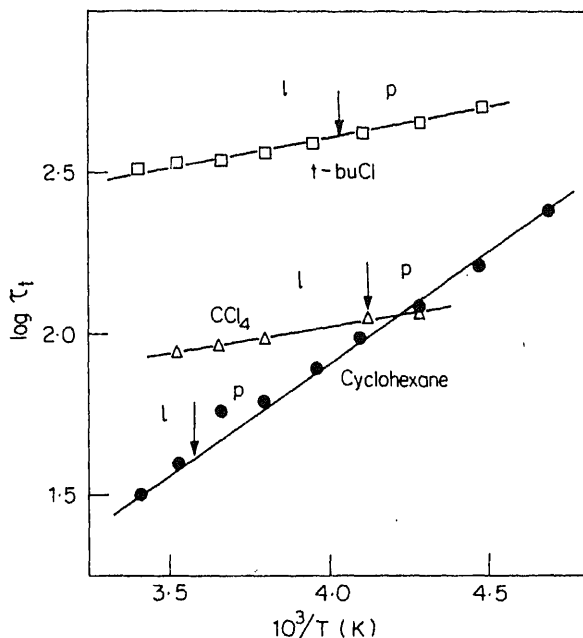


Figure 9. Plots of $\log \tau_t$ (from ESR spectra of the spin probe) versus $1/T$. Arrows show plastic-liquid transitions (after Ganguly *et al* 1981).

trends in figure 10 can be understood in terms of the magnitude of randomization in the plastic state. Whenever ΔS_{cp} or ΔH_{cp} is large, there will be greater randomization in the plastic state and the plastic-liquid range, ΔT_{pl} , will be small. On the contrary, ΔT_{pl} would be large when ΔS_{cp} or ΔH_{cp} is small. It therefore appears that when ΔT_{pl} is small, ΔS_{pl} and ΔH_{pl} would normally be small.

9. Computer simulation studies

Several investigations of the orientationally disordered phases of molecular crystals by computer simulation with various intermolecular potential models have been reported in the literature in recent years. Static and dynamical structure factors obtained from these studies have been compared with those obtained experimentally from neutron scattering studies. Studies on the plastic phases of nitrogen, methane and other substances employing simple atom-atom potentials give good agreement with experiments suggesting thereby that charge-charge interactions do not play a major role

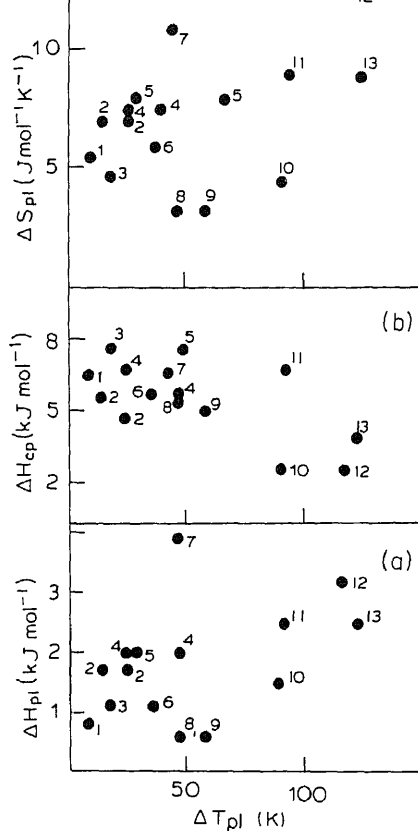


Figure 10. Variation of (a) the ΔH of the plastic-liquid transition with the plastic-liquid range, ΔT_{pl} ; (b) the ΔH of the crystal-plastic transition with the plastic-liquid range, ΔT_{pl} ; (c) the ΔS of the plastic-liquid transition with the plastic-liquid range, ΔT_{pl} (after Ganguly *et al* 1981). The numbers next to the points refer to the compounds in table 1.

have been calculated by molecular dynamics and the results are in satisfactory agreement with experiment. A Monte Carlo study of the quenching of the plastic phase of methane suggests the presence of an orientational glass transition, with an accompanying increase in the lifetime of reorientation of methane molecules (Yashonath and Rao 1983). Furthermore, different cooling rates are found to give rise to different final states.

Recent developments in molecular dynamics and Monte Carlo techniques have made it possible to investigate the structural phase transition from the crystal to the plastic crystal phase (Nose and Klein 1983a; Yashonath and Rao, unpublished results). A molecular dynamics study of the crystal to plastic crystal transition in CF_4 has been reported (Nose and Klein 1983b). Information regarding the molecular arrangement in the high temperature phase has been obtained employing a simple Lennard-Jones potential. A Monte Carlo study of the crystal to plastic crystal phase transition in CCl_4 obtained by isobaric heating has also been carried out (Yashonath and Rao, unpublished results). In figure 11 we show the computer simulated crystalline and

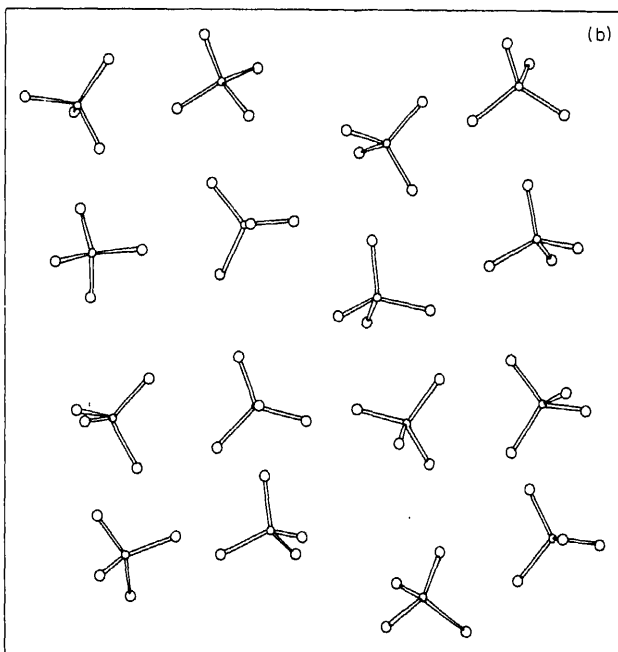
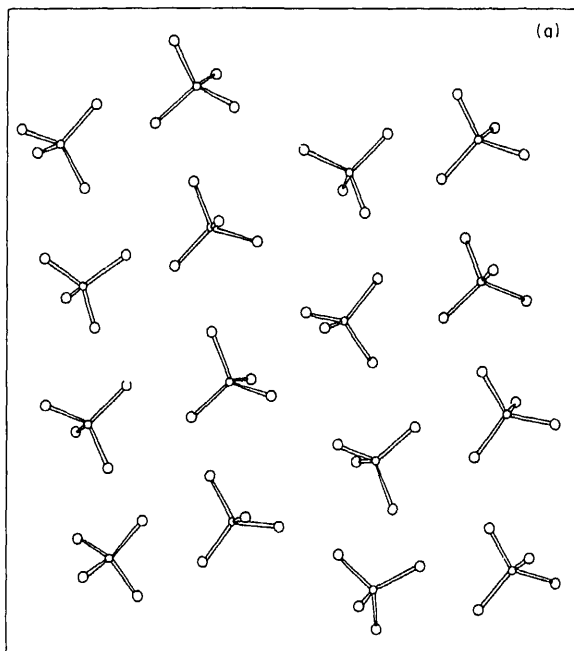


Figure 11. Monte Carlo simulation of CCl_4 (at 1 GPa): (a) crystalline phase at 380 K; (b) plastic phase at 430 K (after Yashonath and Rao unpublished results)

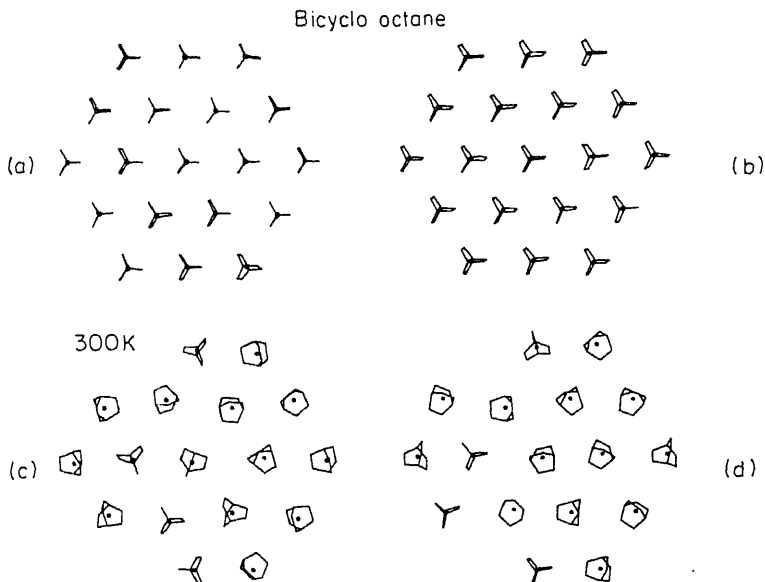


Figure 12. MD simulation of bicyclo octane (after Neusy *et al* 1984): (a) at 50 K (crystalline phase) for the 8-site model; (b) at 50 K (crystalline phase) for the 22-site model; (c) at room temperature (plastic phase) for the 8-site model; (d) at room temperature (plastic phase) for the 22-site model.

plastic phases of CCl_4 . The structural transition in bicyclo-(2.2.2)octane and the computed relaxation time, reorientational dynamics and power spectra associated with translational and rotational motions have been found to be in fair agreement with experiment (Neusy *et al* 1984). In figure 12, the simulated phases of bicyclo octane are shown.

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Particle motion in glasses

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1. Introduction

Glasses are a sub-group of amorphous materials obtained by the quenching of melts and may be distinguished from other non-crystalline materials by the fact that they exhibit the so-called 'glass transition' (Materials Advisory Board 1968). Glasses may be formed from practically all kinds of materials in which the strength of interparticle potentials range from very weak van der Waals (Bondi 1968) through metallic (Cahn 1980) and long range and non-directional ionic (Rao 1980, 1982) to the strongly directional covalent type (Rawson 1967). The stabilities of glasses so formed also vary widely: metallic glasses, for example, are prone to crystallize even before they undergo the glass transition (Angell 1981), while the so-called 'covalent network' glasses, such as B_2O_3 and SiO_2 , are extremely resistant to devitrification (Rawson 1967).

It is well known that glasses retain an imprint of the parent liquid state and hence possess only short range order. The degree of such order, however, varies widely. Recent investigations, particularly those using high resolution electron microscopy (Gaskell *et al* 1979; Bursill *et al* 1981), have suggested the presence of well defined correlations over 50Å regions that could constitute the 'clusters' which characterize the mosaic of a glass. Evidently the particles (throughout this article we understand by the term 'particle', an atom, ion or molecule that is a sufficiently ultimate constituent of a glass) in a glass do not interact with identical potentials and therefore it should be appropriate to describe properties associated with such particles through the use of suitable distribution functions that reflect the distribution of such environments as quantitatively as possible.

The glass transition which marks the ultimate solidification of a supercooled melt is a complex phenomenon that has not been completely understood so far (Rao 1979; Cohen and Grest 1980). The super-cooled melt itself is in metastable equilibrium and a 'real-time' glass transition is a consequence of the system freezing out of this metastable equilibrium. A real glass, consequently, incorporates an excess free energy that manifests itself in a host of relaxation phenomena around the glass transition. The distribution of environments is characterized by a corresponding distribution of the excess free energy, and several irreversible phenomena and responses of glasses to external stimuli may possibly be traced to it. Broadly, all responses that characterize the return to equilibrium of a system perturbed by external stimuli such as alternating electrical or mechanical fields, electromagnetic radiation etc., may be described as 'relaxation phenomena' (Wong and Angell 1976). Information about particle motion in glasses can be extracted from a study of relaxations. It is the purpose of this article to

the methods of investigating particle motions through the use of dielectric and mechanical relaxations, vibrational band shapes, spin resonance absorption relaxations and Mossbauer spectroscopy. In §3 we present some selected studies of glasses using these techniques which have some definitive or novel information related to particle motions. In §4 a rather brief summary of the results of computer experiments bearing on particle motions related to glasses is given and in §5 we present a summary of the conclusions.

2. Methods of studying particle motions

2.1 Dielectric relaxation

Very generally, the dielectric constant ϵ^* is a complex quantity and may be written $\epsilon^* = \epsilon' + i\epsilon''$ (Daniel 1967; Owen 1963). The measured dielectric constant $\epsilon(\omega) = |\epsilon^*(\omega)|$, at frequency ω , may then be written, $\epsilon(\omega) = [(\epsilon')^2 + (\epsilon'')^2]^{\frac{1}{2}}$. The complex nature of $\epsilon^*(\omega)$ implies that the displacement current and applied field are out of phase by an angle δ such that $\epsilon' = \epsilon_s \cos \delta$ and $\epsilon'' = \epsilon_s \sin \delta$ (Daniel 1967; Owen 1963; Stevels 1977), where ϵ_s is the static dielectric constant, and

$$\tan \delta = \epsilon''/\epsilon'. \quad (1)$$

$\tan \delta$ is referred to as the loss tangent or dissipation factor. The term 'loss' implies that the out-of-phase component of the dielectric current which leads to power dissipation is proportional to $\sin \delta$ which for small δ is equal to $\tan \delta$ itself. The dependence of $\epsilon^*(\omega)$ on frequency ω can easily be shown to be (Daniel 1967)

$$\epsilon^*(\omega) = \epsilon_\infty + (\epsilon_s - \epsilon_\infty)/(1 + i\omega\tau), \quad (2)$$

where ϵ_∞ is the high frequency limit of the dielectric constant. τ in (2) is the relaxation time whose significance is clearly seen in figure 1. Equation (2) implies that (Daniel 1967; Owen 1963)

$$\epsilon' = \epsilon_\infty + (\epsilon_s - \epsilon_\infty)/(1 + \omega^2\tau^2) \quad (3)$$

$$\epsilon'' = (\epsilon_s - \epsilon_\infty)\omega\tau/(1 + \omega^2\tau^2) \quad (4)$$

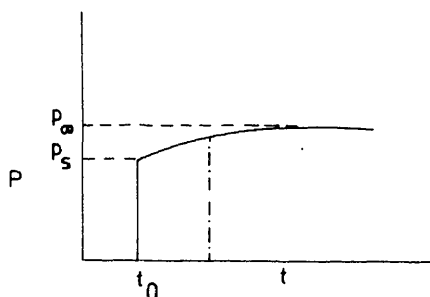


Figure 1. Time dependence of polarisation on applying a static field at t_0 . The relaxation time, τ , is indicated by the line $(- \cdot - \cdot -)$ where $P(\tau) = P_s + (P_\infty - P_s)(1 - 1/e)$.

whereupon $\tan \delta$ may be written

$$\tan \delta = \varepsilon''/\varepsilon' = (\varepsilon_s - \varepsilon_\infty) \omega\tau / (\varepsilon_s + \varepsilon_\infty \omega^2 \tau^2). \quad (5)$$

Equations (2) to (5) are known as the Debye equations and assume the presence of a single relaxation time τ . The variation of ε' and ε'' as a function of $\omega\tau$ is shown in figure 2. An inspection of the above equations or of the figure suggests that ε'' and hence, $\tan \delta$, attains a maximum value when $\omega\tau = 1$ i.e. when $\omega_{\max} = \tau^{-1}$. Similarly, it can be shown that (Owen 1963)

$$\varepsilon''_{\max} = (\varepsilon_s - \varepsilon_\infty)/2 \quad (6)$$

$$\varepsilon'_{\text{mid}} = (\varepsilon_s + \varepsilon_\infty)/2 \quad (7)$$

$$\tan \delta_{\max} = (\varepsilon_s - \varepsilon_\infty) / (\varepsilon_s + \varepsilon_\infty). \quad (8)$$

The full-width at half-maximum (FWHM) of the loss peak is roughly about 1.41 decades of frequency. The frequency corresponding to a maximum in $\tan \delta$, $\omega_{\tan \delta_{\max}}$ is given by (Owen 1963)

$$\omega_{\tan \delta_{\max}} = (\varepsilon_s/\varepsilon_\infty)^{\frac{1}{2}} \tau.$$

In general, however, the concept of a single relaxation time is an over-simplification, particularly for glasses, and the assumption of a distribution of relaxation times is more appropriate (Wong and Angell 1976; Owen 1963). A relaxation time spectrum may be represented by $G(\tau)$ such that $\int_0^\infty G(\tau) d\tau = 1$ (Owen 1963). The Debye equations (2–5) get modified appropriately and ε^* may then be written as (Owen 1963)

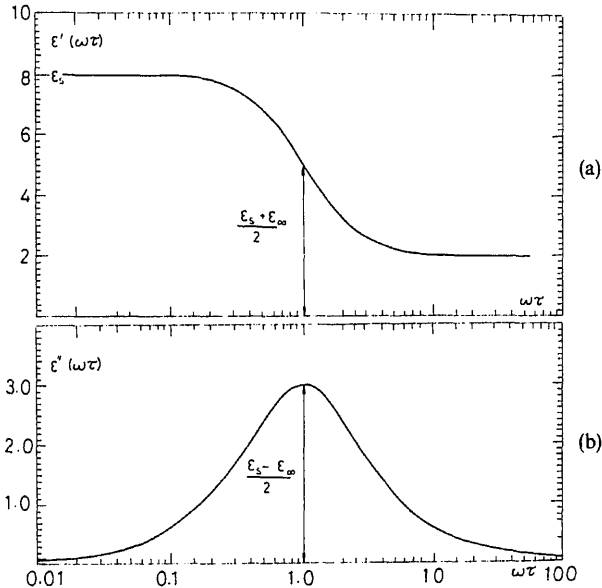


Figure 2. (a) The real part of ε^* as a function of $\log \omega\tau$ for a dielectric with a single

Many types of distribution functions have been used; historically the oldest corresponds to a Gaussian probability function (Wagner 1913; Owen 1963) where

$$G(\tau) d\tau = (b/\pi)^{1/2} \exp(-b^2 z^2). \quad (10)$$

In this equation b is a constant and z corresponds to $\ln(\tau/\tau_0)$ where τ_0 is the peak value of the relaxation time. It is implicit in the use of a Gaussian that the intrinsic relaxation time τ_0 is broadened by an infinite number of independent causes. The breadth of the distribution increases rapidly as b decreases below 1. The introduction of a relaxation time distribution does not, however, materially alter $\omega_{\max}$ which still corresponds to $(\tau_0)^{-1}$ and the total dispersion in ϵ' remains equal to $(\epsilon_s - \epsilon_\infty)/2$ (Owen 1963). Fuoss and Kirkwood (1941) have considered the possibility of deriving distribution functions based on experimental ϵ'' vs ω plots using transformation methods. Cole and Cole (1941) obtained a distribution function based on an empirical modification of the complex form of the Debye equation

$$\epsilon^* = (\epsilon_s - \epsilon_\infty) / [1 + (i\omega\tau_0)^{1-\alpha}] \quad (11)$$

where α , $0 \leq \alpha \leq 1$, is a constant related to the width of the distribution. Another distribution function of an empirical origin that has been used to analyse asymmetric Cole-Cole plots (see later) is the Davidson-Cole function (Davidson and Cole 1951). It is yet another modification of the Debye equation and is written

$$\epsilon^* - \epsilon_\infty = (\epsilon_s - \epsilon_\infty) / (1 + i\omega\tau_0)^\beta \quad (12)$$

where β , $0 \leq \beta \leq 1$ is a constant similar to α .

The origin of the distribution functions has been discussed by many authors notable of whom are Kauzmann (1942) and Fröhlich (1958). Kauzmann (1942) has applied the theory of chemical rate processes to the problem of dielectric relaxation times. In this approach the distribution of relaxation times originate from thermal fluctuations that cause changes in the environments of the relaxing dipoles (Owen 1963). As a consequence of such changes, a symmetric distribution of barriers results about the barrier height corresponding to the unperturbed state. Fröhlich's (1958) analysis is more relevant to glasses in that it recognises the presence of a distribution of site symmetries and dipole environments in a glass. This very naturally leads to a relaxation time spectrum since $\tau_0 = \tau'_0 \exp(-\Delta H/kT)$. A distribution in ΔH , therefore, may be regarded as the origin of the relaxation time spectrum in this approach. An advantage in Fröhlich's approach is that irrespective of the initial distribution in ΔH , an increase in temperature should lead to narrowing of the relaxation time spectrum. This, of course, implies either that τ'_0 is unaffected or that ΔH and $\ln \tau'_0$ vary proportionately, a feature verified in a number of systems.

Dielectric data is often represented using the Cole-Cole plot which is simply an Argand diagram (or a complex plane representation) of the real and imaginary components of ϵ^* (Cole and Cole 1941; Daniel 1967; Owen 1963). In the simple case of a Debye dielectric, the Cole-Cole plot (figure 3a) is a simple semi-circle terminated at ϵ_∞ and ϵ_s on the real axis (Daniel 1967; Owen 1963). The semi-circle itself is the locus of ϵ^* values each for a given value of $\omega\tau_0$. $\epsilon''_{\max}$ corresponds to $\omega\tau_0 = 1$ and the equation of

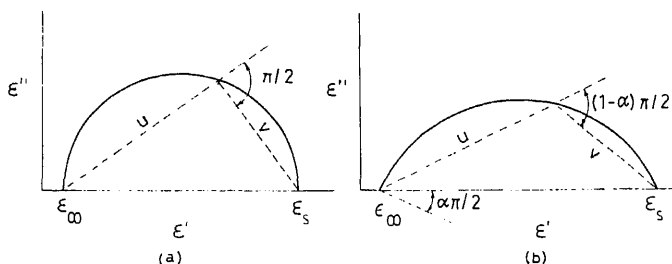


Figure 3. The Cole-Cole representations for (a) the Debye dielectric and (b) for a dielectric with a distribution of relaxation times (after Owen 1963).

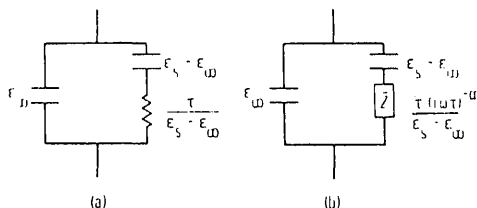


Figure 4. Equivalent circuit representations of (a) a Debye dielectric and (b) a dielectric with a distribution of relaxation times (after Owen 1963).

the semi-circle may be obtained by combining the Debye equations (Daniel 1967)

$$[\epsilon' - (\epsilon_\infty + \epsilon_s)]^2/2 + (\epsilon'')^2 = (\epsilon_s - \epsilon_\infty)^2/4. \quad (13)$$

Now, considering any two vectors $\mathbf{u}$ and $\mathbf{v}$ within the semi-circle one sees that the two are necessarily perpendicular to each other. The following equations may also be easily derived (Daniel 1967)

$$\mathbf{u} \cdot \mathbf{v} = (\epsilon_s - \epsilon_\infty) \quad (14a)$$

and

$$\mathbf{u} = \epsilon' - \epsilon_\infty + i\epsilon'' \quad (14b)$$

Using the definition of ϵ' (equation (3)) it is clear that

$$\mathbf{v} = \mathbf{u}i\omega\tau \quad (14c)$$

The generalized Cole-Cole distribution which takes into account the existence of a distribution of relaxation times simply amounts to modifying (14c) as (Daniel 1967)

$$\mathbf{v} = \mathbf{u}(i\omega\tau_0)^{1-\alpha} \quad (15)$$

The Cole-Cole plot for such a distribution is shown in figure 3b. It is the arc of a circle whose centre lies below the ϵ' axis and the line joining the centre of the semi-circle to the origin is perpendicular to the ϵ' axis. (Daniel 1967, eqn (7)).

gets charged instantaneously while the charging of $(\epsilon_s - \epsilon_\infty)$ may be regarded as being prevented by a resistance equal to $\tau/(\epsilon_s - \epsilon_\infty)$. In figure 4b the impedance corresponds to $\tau(i\omega\tau)^{-1/2}/(\epsilon_s - \epsilon_\infty)$.

2.2 Mechanical relaxation

The response of a glass to cyclic mechanical stress may also be treated similarly (Litovitz and Davis 1965; Philipoff 1965). It is however, conventional to treat the behaviour of the modulus rather than the compressibility and this may be regarded as being equivalent to the dielectric constant. For the propagation of a shear wave in a viscoelastic medium, the shear modulus G^* may be written as (Wong and Angell 1976; Litovitz and Davis 1965)

$$G^* = G' + iG'' = G' + i\omega\eta_s \quad (16)$$

where ω is the angular frequency and η_s is the shear viscosity. When the static shear modulus is zero (as relevant to a glass above glass transition)

$$G' = G_\infty \omega^2 \tau_s^2 / (1 + \omega^2 \tau_s^2) \quad (17)$$

and

$$G'' = G_\infty \omega \tau_s / (1 + \omega^2 \tau_s^2) = \omega \eta_s. \quad (18)$$

At low frequencies, $\eta_s = G_\infty \tau_s$. In mechanical relaxation studies it is often convenient to define a complex longitudinal modulus $M^* = M' + iM'' = K^* + 4G^*/3$ where K^* is the bulk modulus and G^* is the shear modulus. Litovitz and Davis (1965) have shown that M' and M'' may be approximated as

$$M' = \rho v^2 \quad \text{and} \quad M'' = 2\rho v^3 / \alpha \omega \quad (19)$$

where α is the absorption coefficient and ρ and v are the density of the material and the velocity of sound, respectively. The absorption coefficient, α , may also be related to η using (Litovitz and Davis 1965)

$$\alpha \lambda = \pi \omega [(\eta_v + 4\eta_s/3)] / K_0 \quad (20)$$

where K_0 is the low frequency ('static') bulk modulus, η_v is the volume viscosity and λ the wave length of the ultrasonic wave. It is common in ultrasonic studies to relate the various moduli to acoustic impedances. The complex shear impedance, Z_s , for instance, may be written, (Litovitz and Davis 1965)

$$Z_s = \rho v_c = \rho [(1/v_s) + (\alpha/i\omega)]^{-1} = R_x + iX_s \quad (21)$$

using this, G' and G'' may be expressed as (Litovitz and Davis 1965)

$$G' = (R_s^2 - X_s^2) / \rho \quad (22a)$$

and

$$G'' = 2R_s X_s / \rho. \quad (22b)$$

Since an applied mechanical disturbance propagates both as longitudinal and shear waves, two theoretical models, namely, Maxwell and Voight models (Philipoff 1965) are used to analyse the mechanical relaxations. In Maxwell's model, the total deformation is taken as the sum of the viscous and elastic components while the shear stresses for the

deformations are considered to be equal. Equations (16) to (20) are based on Maxwell's model.

The discussion so far has been limited to a system with a single relaxation time. In real situations, as pointed out earlier, a distribution of such times exists and these relaxation times are described in terms of a reduced parameter, τ_s/τ_s' . Two such distributions often used correspond to the symmetric Gaussian and the asymmetric Davidson–Cole distributions. In the presence of these distributions, K' , K'' , η_v , G' , G'' and η_s are defined by the integrals given in table 1.

In this article our intention is to focus on particle motions in the glassy state itself. As such, an analysis of the frequency dispersion of the shear modulus in the supercooled liquid is only of marginal interest to this article. Mechanical relaxation in the low-frequency region studied in internal friction measurements is more informative with respect to particle motions in glass.

We may note in passing that while the analyses of dielectric data are often performed using complex susceptibility, analyses of mechanical relaxations are done using complex modulus. More recently, however, the modulus representation is in vogue even in dielectric relaxation studies. This transformation is easily achieved by defining a dielectric modulus $M^* = M' + iM'' = 1/\epsilon^*$. The resulting expressions are similar to those for mechanical relaxation (Wong and Angell 1976; Macedo *et al* 1972). In situations where the d.c. conductivity is large and is comparable to the a.c. conductivity, it is often advisable to treat the corrected conductivity ($\sigma_{a.c.} = \sigma_{total} - \sigma_{d.c.}$) itself as a complex quantity so that (Grant 1958; Daniel 1967)

$$\sigma^* = \sigma' + i\sigma'' = i\omega(\epsilon' - i\epsilon'') \quad (23)$$

Mechanical loss at low (10^{-2} Hz to 50 kHz) frequencies is often called internal friction which is identical to the loss angle or $\tan \delta$ (Zdaniewski *et al* 1979). In this long-wavelength region where power dissipation is primarily through viscous flow, mechanical relaxation is advantageously described (Zdaniewski *et al* 1979) using the

Table 1. Mechanical properties for distributions of relaxation times.

$K' = K_0 + K_r \int_0^\infty k(\tau/\tau_v') \omega^2 \tau^2 d(\tau/\tau_v') / (1 + \omega^2 \tau^2)$	$G' = G_\infty \int_0^\infty \omega^2 \tau k(\tau/\tau_s') d(\tau/\tau_s') / (1 + \omega^2 \tau^2)$
$K'' = K_r \int_0^\infty k(\tau/\tau_v') \omega \tau d(\tau/\tau_v') / (1 + \omega^2 \tau^2)$	$G'' = G_\infty \int_0^\infty \omega \tau k(\tau/\tau_s') d(\tau/\tau_s') / (1 + \omega^2 \tau^2)$
$\eta_v = K_r \int_0^\infty k(\tau/\tau_v') \tau d(\tau/\tau_v') / (1 + \omega^2 \tau^2)$	$\eta_s = G_\infty \int_0^\infty \tau k(\tau/\tau_s') d(\tau/\tau_s')$

Distribution functions used

(i) *Gaussian:*

$$k(\tau/\tau_{s(v)}) = b/\pi^{1/2} \cdot \tau_{s(v)}/\tau \cdot \exp[-b \ln(\tau/\tau_{s(v)})]^2 \quad 0 < \tau < \infty$$

(ii) *Davidson–Cole:*

compliances S_u and S_r where the subscripts u and r denote the unrelaxed and relaxed states. S_u can be written $S_u = 1/C_u$ and $S_r = 1/C_r$ in terms of the stiffness constants C_r and C_u . The complex compliance is $S^* = S' - iS''$, so that

$$\tan \delta = (S_r - S_u)/(S_r + S_u \omega^2 \tau^2) \quad (24)$$

which may be compared with (5) in the dielectric case. For many solids, the relaxation strength, $\Delta = (S_r - S_u)/S_u$, is far less than 1 so that

$$\tan \delta = \Delta \omega \tau / (1 + \omega^2 \tau^2) \quad (25)$$

and $\tan \delta$ is therefore a symmetrical function of $\log \omega \tau$ centred about $\omega \tau = 1$. $\tan \delta$ is a measure of the absorption of vibrational energy in a solid (Fitzgerald 1951) and is also referred to as Q^{-1} , where Q is the quality factor. Experimentally it is determined by measuring the logarithmic decrement of vibrational amplitude of a freely vibrating solid, ϕ , where $\phi = \ln(A_0/A_n)$, $\tan \delta$ is then given by

$$\tan \delta = Q^{-1} = 2.303 \phi / n\pi, \quad (26)$$

where n is the number of cycles.

One of the basic modes of particle motion is vibrational. In the formalism that we have employed so far for dielectric and mechanical responses the expressions were relevant for time-scales far larger than vibrational time-scales. These time-scales, however, are themselves accessible to far infrared (FIR) spectroscopy (Wong and Angell 1976). The nature of absorption of energy from the impressed field has to be treated in the frame-work of a forced harmonic oscillator (Dekker 1967). If ω_0 is the frequency of a harmonic oscillator that is subjected to an alternating field of frequency ω , it can be shown that the complex dielectric constant arising from the polarization induced by elastic displacements is (Dekker 1967)

$$\epsilon^* = 1 + [4\pi N e^2 / m ((\omega_0^2 - \omega^2) + i\gamma\omega)]. \quad (27)$$

In (27) N , e , m , and γ are the number of particles per unit volume, the charge and mass of the particle and the damping constant (in units of ω^{-1}) respectively. The real and imaginary components may now be seen to be (Dekker 1967)

$$\epsilon' = 1 + \{4\pi N e^2 (\omega_0^2 - \omega^2) / [(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2]\} \quad (28)$$

$$\epsilon'' = 4\pi N e^2 (\gamma \omega) / m [(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2]. \quad (29)$$

It may be noted that absorption takes place only in the presence of the damping constant, γ , and this type of absorption is called 'resonant absorption'. While the absorption, i.e. ϵ'' or $\tan \delta$, peaks around ω_0 as in the case of relaxation, ϵ' (or more appropriately, $\epsilon' - 1$) exhibits an anomalous dispersion (Lovell *et al* 1976). In solids it is more accurate to use ω_0 which is corrected for the presence of the Lorentz field and this is achieved by writing ω_1 for ω_0 where $\omega_1 = \omega_0^2 - (4\pi n e^2) / 3m$ (Dekker 1967).

Since refractive index and dielectric constant are related, we can consider resonance

It is conventional to measure absorbance $\alpha(\omega)$ in the high-frequency regime and $\alpha(\omega)$ is related to $\epsilon''(\omega)$ by the expression (Wong and Angell 1976)

$$\alpha(\omega) = \omega \epsilon''(\omega) / cn(\omega) \quad (32a)$$

where c is the velocity of light. ϵ'' may be related to the conductivity of the material through the relation (Wong and Angell 1976)

$$\sigma(\omega) = \omega \epsilon_0 \epsilon''(\omega) \quad (32b)$$

where ϵ_0 is the permittivity of free space. Using this expression it is possible to evaluate conductivities at very high frequencies using values of the absorbance.

2.3 Vibrational spectroscopy

Particle motion in glasses, especially around the glass transition, can be profitably investigated using vibrational spectroscopy (Yarwood and Arndt 1979; Lascombe 1974). The band widths in IR and Raman spectroscopies, in particular, are influenced profoundly by molecular interactions. In the Schrödinger picture, transitions are regarded as taking place between well-defined states but in the Heisenberg approach attention is focussed on the time-evolution of these transitions so that the intensity of the band can be related to the appropriate correlation functions (Gordon 1965; Yarwood and Arndt 1979). It may be noted that both auto- and cross-correlation functions affect the band-shape but the latter are important only when motion is highly cooperative in nature. The shape of the correlation function, in principle, contains complete information about particle motion. Detailed accounts of the origin of band shapes and their analysis has been given by a number of authors (Gordon 1965, 1968; Bratos and Maréchal 1971; Young and Jones 1971; Nafie and Peticolas 1972; Bartoli and Litovitz 1972; Bailey 1974; Lascombe 1974; Yarwood and Arndt 1979). The two auto-correlation functions of interest to us are $\langle \mathbf{Q}_i(0) \cdot \mathbf{Q}_i(t) \rangle$ and $\langle \mathbf{u}_i(0) \cdot \mathbf{u}_i(t) \rangle$ where the $\mathbf{Q}$'s are the normal coordinates of the i th molecule and the $\mathbf{u}$'s are the unit vectors along the transition moment corresponding to the $\mathbf{Q}$'s. If the normalised IR band intensity is written $\hat{I}_{\text{IR}}(\omega)$, a Fourier transform of the band is related to the correlation function by (Yarwood and Arndt 1979)

$$\begin{aligned} \Phi_{\text{IR}}(t) &= \phi_v(t) \phi_{\text{IR}}(t) = \langle \mathbf{Q}_i(0) \cdot \mathbf{Q}_i(t) \rangle \\ \langle P_1[\mathbf{u}_i(0) \cdot \mathbf{u}_i(t)] \rangle &= \int \hat{I}_{\text{IR}}(\omega) \exp(i\omega t) d\omega, \end{aligned} \quad (33)$$

where $P_1 = \cos \theta_i(t)$ is the first order Legendre polynomial and $\theta_i(t)$ is the angle between the transition dipoles of the i th molecule at times 0 and t . In the case of Raman spectra obtained using a vertically polarized light source we have to consider both the vertically polarized scattered intensity (I_{VV}) and the horizontally polarized scattered intensity (I_{VH}). I_{VV} and I_{VH} contain information with respect to different correlation times and are related to isotropic ($I_{\text{iso}}(\omega)$) and anisotropic ($I_{\text{aniso}}(\omega)$) scattering intensities through the following expressions (Bartoli and Litovitz 1972).

Corresponding correlation functions are given by (Yarwood and Arndt 1979)

$$\Phi_{\text{iso}}(t) = \phi_v(t) = \langle \mathbf{Q}_i(0) \cdot \mathbf{Q}_i(t) \rangle = \int_{\text{band}} I_{\text{iso}}(\omega) \exp(i\omega\tau) d\omega \quad (35)$$

$$\begin{aligned} \Phi_{\text{aniso}}(t) &= \phi_v(t) \phi_{2R}(t) = \langle \mathbf{Q}_i(0) \cdot \mathbf{Q}_i(t) \rangle \langle P_2[\mathbf{u}_i(0) \cdot \mathbf{u}_i(t)] \rangle \\ &= \int_{\text{band}} I_{\text{aniso}}(\omega) \exp(i\omega\tau) d\omega, \end{aligned} \quad (36)$$

where $P_2 = \frac{1}{2}[3 \cos^2 \theta_i(t) - 1]$ is the second order Legendre polynomial. The auto correlation function corresponding to $\langle \mathbf{Q}_i(0) \cdot \mathbf{Q}_i(t) \rangle$ is known as the vibrational relaxation function (van Konynenburg and Steele 1975; Rothschild 1976; Doge *et al* 1977). While $\langle \mathbf{u}_i(0) \cdot \mathbf{u}_i(t) \rangle$ represents the reorientational correlation function (Yarwood and Arndt 1979). From the above equations it is obvious that

$$\phi_v^{\text{iso}}(t) = \Phi_{\text{iso}}(t) \quad (37a)$$

$$\phi_{1R}(t) = \Phi_{1R}(t)/\Phi_{\text{iso}}(t) \quad (37b)$$

$$\phi_{2R}(t) = \Phi_{\text{aniso}}(t)/\Phi_{\text{iso}}(t). \quad (37c)$$

In arriving at the above equations, it is assumed that the effect of a finite slit-width has been taken into account. Ignoring slit width effect is strictly incorrect.

A plot of the correlation function against time can be used to obtain the correlation time, τ_c which is defined by $\phi(\tau_c) = \phi(0)/e$ (figure 5). The correlation times obtained

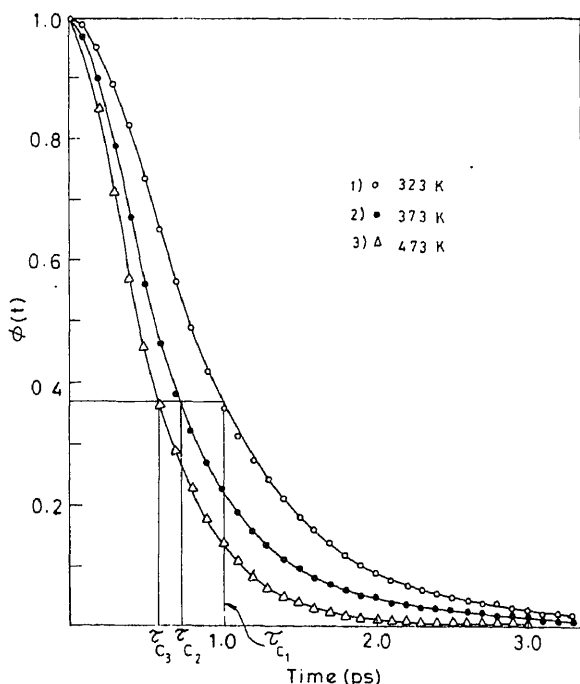


Figure 5. Variation of $\phi(t)$ with t for sulphate glasses at the temperatures indicated (see

thus from ϕ_{1R} (from IR) and ϕ_{2R} (from Raman) are the reorientational times. The correlation function $\langle \mathbf{u}_i(0) \cdot \mathbf{u}_i(t) \rangle$ is also often designated $\langle \mathbf{u}_i^{(2)}(0) \cdot \mathbf{u}_i^{(2)}(t) \rangle$ indicating that it is related to roto-diffusive motion.

Vibrational spectra can also be analysed in terms of band moments (Gordon 1965, 1968; Bailey 1974) since the correlation functions can be expanded in terms of a series of the moments. For a classical system consisting of relatively heavy molecules (Bailey 1974), the odd moments can be ignored and the correlation function may be written (Yarwood and Arndt 1979)

$$\phi(t) = 1 - [M_2 t^2/2!] + [M_4 t^4/4!] - [M_6 t^6/6!] + \dots \quad (38a)$$

where

$$M_n = \int_{\text{band}} (\omega - \omega_0)^n I(\omega - \omega_0) d\omega / \int_{\text{band}} I(\omega - \omega_0) d\omega. \quad (38b)$$

Many models of rotational and roto-diffusive motions have been described in the literature. Debye considered only small angle diffusive steps in his model (Debye 1929). Gordon developed a model of extended diffusion along similar lines (Gordon 1966). Gordon's M and J diffusion models correspond to cases where only orientations are randomized upon collision (M diffusion) and where the length of the angular momentum vector is also randomized (J diffusion). These models have been applied extensively and have been discussed by Kivelson and McClung (1968). The various τ values such as $\tau_j, \tau_\theta^1 \equiv \tau_{1R}$ and $\tau_\theta^2 \equiv \tau_{2R}$ are related amongst themselves. In the perturbed limit of a free rotor, τ_θ (corresponding to the correlation time from the Debye model) is approximately equal to τ_j (Yarwood and Arndt 1979) and is itself approximated by the Stokes-Einstein relationship,

$$\tau_\theta \simeq 4\pi\eta a^3/3kT, \quad (39)$$

where η is the viscosity and a is the molecular radius. On the other hand, Kivelson and McClung (1968) have shown that τ_j for a spherical top molecule is given by

$$\tau_j = I_\alpha/8\pi K r_\theta^3 \eta, \quad (40)$$

where I_α is the moment of inertia (referred to the α th axis), K is a constant between 0 and 1 whose value is determined by the anisotropy of the molecular potential and r_θ is the mean molecular radius. Equation (40) shows that $\tau_j \propto 1/\eta$.

2.4 Spin resonance studies

In glasses which contain either paramagnetic species or nuclei with non-zero spin, spin resonance experiments are of value in studying particle motions. A nuclear spin precesses about the axis of an applied magnetic field at its Larmor frequency, $\omega = \gamma H$, where γ is the nuclear gyromagnetic ratio and H is the applied field. The variation of the magnetization $\mathbf{M}$ of a material with time is given by (Pake and Estle 1973; Carrington and McLachlan 1967),

$$d\mathbf{M}/dt = \gamma \mathbf{M} \times \mathbf{H}. \quad (41)$$

The relaxation of magnetization along the three coordinate axes is given by the following equations known as the Bloch equations (Bloch 1946; Pake and Estle 1973)

relaxation times respectively and M_0 is the equilibrium magnetization. The Bloch equations are easily solved for the condition that an oscillating magnetic field is superimposed upon the static field. Expressions for the real, χ' and imaginary χ'' , parts of the complex magnetic susceptibility $\chi^* = \chi' - i\chi''$ are given by the following equations (Carrington and McLachlan 1967; Schumacher 1970),

$$\chi'(\omega) = \frac{1}{2}\chi_0\omega_0 T_2(\omega - \omega_0)T_2/[1 + (\omega - \omega_0)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2] \quad (43a)$$

$$\chi''(\omega) = \frac{1}{2}\chi_0\omega_0 T_2/[1 + (\omega - \omega_0)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2] \quad (43b)$$

ω and ω_0 are defined by $\omega = \gamma H$ and $\omega_0 = \gamma H_0$ where H_0 is the value of the field at the absorption maximum ($\chi''_{\max}$). T_2 is related to the line-width and is given by (Poole and Farach 1971)

$$T_2 = 2/\gamma\Delta H_{1/2}^0 = 2/\sqrt{3}\gamma\Delta H_{pp}^0, \quad (44)$$

where ΔH_{pp}^0 is the peak-to-peak line-width in the derivative spectrum (assuming a Lorentzian profile of absorption). Determination of T_1 , however, is more complex and needs saturation experiments. It may then be determined using ΔH vs P plots where P is the rf power. Knowing the slope, T_1 may be determined using the formula, $T_1 = \text{slope}/\gamma^2 T_2$ (Poole and Farach 1971). The origins of the line-broadening in magnetic resonance experiments generally fall into two categories *viz*, homogeneous and heterogeneous band-broadening. Homogeneous broadening occurs when the spin-levels between which the transition takes place are not clearly defined and are intrinsically broadened. This may occur either because of spin-spin dipolar interactions or spin-lattice interactions. 'Inhomogeneous broadening', however, describes an envelope of individual resonance peaks which are (shifted from their true position particularly by magnetic field inhomogeneities (Poole and Farach 1971). The dipolar interactions may be treated using the dipolar Hamiltonian, H_{DD} which (for the case of nuclear spin interactions) is given by (Carrington and McLachlan 1967),

$$H_{DD} = g_N^2 \beta_N^2 \left[\frac{\mathbf{I}_1 \cdot \mathbf{I}_2}{r^3} - 3 \frac{(\mathbf{I}_1 \cdot \boldsymbol{\gamma})(\mathbf{I}_2 \cdot \boldsymbol{\gamma})}{r^5} \right], \quad (45)$$

which describes the interaction between two identical magnetic moments $g_N \beta_N I$ separated by a distance r . This line broadening mechanism dominates in many solids but is largely averaged out in fluids. Using a Boltzmann distribution for the population of the spin states it can be shown that (Carrington and McLachlan 1967),

$$(1/T_1) = W_1 + 2W_2, \quad (46)$$

where W_1 and W_2 are transition probabilities involving matrix elements of H_{DD} . Spins in the neighbourhood of the excited spin that are involved in random motion (both rotational and translational) cause random fluctuations at the site of the excited spin. An auto-correlation relaxation time, τ_c , of the random fluctuations can be defined that determines the value of T_1 and T_2 (Carrington and McLachlan 1967).

Of greater importance in glass is motional narrowing that occurs in NMR studies. We have already noted that T_2 is inversely proportional to $\Delta H_{1/2}^0$ or, equivalently (Wong and Angell 1976),

$$T_2^{-1} = \Delta\omega_0^2 \tau, \quad (47)$$

This type of narrowing has been treated by Bloembergen *et al* (1948) whose theory has been modified (Gutowsky and McGarvey 1952; Gutowsky and Pake 1950) to relate ν_j the jump frequency to $\Delta\omega$

$$\nu_j = (2\pi\tau)^{-1} = \alpha\Delta\omega/\tan\left(\frac{\pi}{2}\left(\frac{\Delta\omega}{\Delta\omega_0}\right)^2\right), \quad (48)$$

where α is a constant of the order of unity and $\Delta\omega_0$ is the line width when there is no motional narrowing. Since ν_j itself can be treated as a thermally activated quantity (Lidiard 1957; Poole and Farach 1971),

$$\nu_j = \nu_0 \exp(-E_a/kT). \quad (49)$$

The relation between τ_c and T which leads to band width narrowing with increasing temperature is at once apparent. A phenomenological model for motional narrowing has been developed by Hendrickson and Bray (1973) based on a two-state model. This yields the expression

$$\ln\left(\frac{1}{\Delta\omega} - \frac{1}{\Delta\omega_0}\right) = (-E_a/kT) - \ln(1/B - 1/\omega_0), \quad (50)$$

where B is the line-width associated with the excited state and may be related to the nature of the motion involved.

In ESR spectroscopy line-broadening mechanisms are again the spin-spin and spin-lattice interactions. The spin-lattice interaction is characterized by the relaxation time T_1 and may be looked upon as arising from two causes. In the first, the spin experiences magnetic field variations due to the dipolar fluctuations from lattice vibrations. In the second mechanism, proposed by Kronig (1939) and van Vleck (1939), variations in the local electrostatic fields are regarded as affecting the orbital motion of the electrons which in turn perturbs the energy levels in the paramagnetic species. This perturbation is sensed by the spin through spin-orbit coupling, thus providing a mechanism for spin relaxation. In general, $1/T_1$ is proportional to the square of the spin-orbit coupling constant, λ , and inversely proportional to the axial field splitting, δ , raised to a high power. The temperature dependence of spin-lattice coupling can also be quite different in different temperature ranges (Ayscough 1967).

Spin-spin relaxation is more directly explained. This may occur either through direct exchange in which case T_2 should be directly proportional to the exchange interaction energy J (or, $\omega_e = J/h$ the so-called exchange frequency) and inversely proportional to the square of the dipolar interaction E_{dd} (Ayscough 1967). Spin-spin coupling could also take place *via* the magnetic field of the spins themselves.

In solutions, however, relaxation of spin-half free-radicals and paramagnetic ions is governed by the anisotropy of the g -tensor, by spin-orbit interactions and also by dipolar coupling with the magnetic nuclei, (Carrington and McLachlan 1967; Ayscough 1967; Poole and Farach 1971; Pake and Estle 1973). It has been shown (Carrington and McLachlan 1967) that for the case of the anisotropic g -tensor T_1 and T_2 are governed by the relations

$$1/T_1 = (g' : g') \beta^2 H_0^2 [12\tau_c / (1 + \omega_0^2 \tau_c^2)] / 60\hbar^2 \quad (51a)$$

$$1/T_2 = (g' : g') \beta^2 H_0^2 [8\tau_c + 6\tau_c (1 + \omega_0^2 \tau_c^2)] / 60\hbar^2,$$

where $(g' : g')$ denotes the inner product of the tensor with itself, $(g' : g') = \sum_{ijk} g'_{ijk} g'_{ijk}$. The formulation of the relaxation mechanisms for paramagnetic ions and free-radical spins greater than half is, however, more complex and detailed discussions are to be found elsewhere (Poole and Farach 1971).

2.5 Mossbauer spectroscopy

Mossbauer spectroscopy can also be employed very usefully to investigate particle motions in glasses. The particle motion is directly reflected in the Lamb-Mossbauer factor or the recoil-free fraction, f , which is given by (Wertheim 1964)

$$f = \exp(-4\pi^2 \langle x^2 \rangle / \lambda^2),$$

where $\langle x^2 \rangle$ is the mean square amplitude of vibration in the direction of gamma-ray emission averaged over a time-interval equal to the life-time of the excited nucleus, and λ is the wavelength of the gamma ray photon. Since $\langle x^2 \rangle$ reflects the average displacement of particles from their mean position a temperature-variable study of Mossbauer spectra of glasses should be quite informative particularly in the neighbourhood of the glass transition (Champeny 1979) where large thermal disturbances in particle positions may be expected. Other parameters such as isomer shift and quadrupole splitting also reflect the effect of motion but these effects are rather subtle and do not allow unequivocal interpretation by themselves.

3. Experimental studies

3.1 Dielectric response

Amongst the various methods used to study relaxation phenomena in glasses, dielectric relaxation is probably one of the most widely used (Owen 1963; Day 1974; Day 1977). We have already noted that dielectric relaxation is both temperature and frequency dependent so that one might expect to investigate relaxation behaviour by varying either temperature or frequency. The impressive amount of data gathered to date, far, does in fact demonstrate that both the variables have been exploited. The various sources of dielectric loss in glasses are (a) migration losses and (b) deformation losses (Stevens 1957; Owen 1963). It is to be expected that deformation losses are associated with the dipolar mechanism of charge storage and should, therefore, be common to molecular, covalent network and other types of glasses. Migration losses, on the other hand, should play a large role in modified network and in purely ionic glasses. In semiconducting glasses, electron hopping from site to site is the dominant source of dielectric loss (Lakatos and Abkowitz 1971; Thurzo 1975; Namikawa 1976; Bayoumi and MacCrone 1976; Mansingh *et al* 1972, 1975, 1976, 1978).

The subject of the dielectric behaviour of glasses has been reviewed excellently by Owen (1963) and more recently by Stevens (1977). In their study of pure fused silica, Mahle and McCammon (1969) have found a dielectric loss peak at 1 kHz and which they attributed to the motion of network oxygens. Many technically important glasses which contain cations in a silicate or a borosilicate network exhibit dielectric

silicate glasses are approximately equal, indicating that the same mechanism is operative in both cases. A more recent review by Namikawa (1975) of a large number of silicate glasses, however, indicates that dielectric behaviour of glasses may actually be grouped in three categories. In the first category, a Maxwell-Wagner (Daniel 1967; Wagner 1914; Maxwell 1954) type of behaviour is postulated in which ions move over short distances with low activation energies. As a consequence, the barriers to a.c. and d.c. conductivities are vastly different. In the other two categories, ionic motion occurs over larger distances and the barriers to a.c. and d.c. conductivity are similar. The two categories, however, may be distinguished by the magnitude of a correlation factor, p , where p is defined as the ratio of $\sigma_{\text{d.c.}}$ to $\epsilon_0(\epsilon_s - \epsilon_\infty)\omega_m$, where ω_m is the frequency at the loss maximum ($\sigma_{\text{d.c.}}$ and ω_m are referred to the same temperature). In figure 6a, b and c the behaviour of ϵ'' as a function of $\log f$ is shown for the three categories, and some examples are listed in table 2. Semiconducting glasses such as barium phosphotungstates also appear to exhibit migration losses very similar to those corresponding to long range diffusion of ions (Namikawa 1975).

The mechanism of ionic transport in glasses has been discussed by many workers using different models. Stevels and co-workers (Haven and Stevels 1956) have considered several mechanisms by which Na^+ can be transported in glasses such as free transport, vacancy transport, interstitial transport and interstitialcy transport corresponding both to short and long distances. Urnes (1967) has considered the possibility of a Grotthus-type mechanism being operative in glasses under the action of an electrical field. Both these models have, nonetheless, been criticized though they are capable of explaining at least qualitatively, the discrepancy between measured values of the diffusion coefficient, D , and those derived using the Nernst-Einstein equation

$$D/N = kT/ne^2. \quad (53)$$

A correlation factor, f , which is a measure of this discrepancy may be defined through the relation $D/N = fkT/ne^2$. Doremus has suggested that the deviation of f from unity is due to very fine scale phase separation. The presence of sub-microscopic heterogeneity has also been suggested by Terai and Hayami (1975). The low values of f that have been observed can occur when preferential paths are provided by such heterogeneities. In these models, the mechanism of d.c. conductivity would itself require the presence of both the fine scale phase separation and of different ranges of jump distances and would also require the operation of defect interstitialcy mechanisms. These facets of d.c. conductivity may be compared with several features of a.c. conductivity mentioned earlier. Thus materials where f is very different from unity should generally show Maxwell-Wagner losses.

Most alkali silicate glasses conform to a distribution of relaxation times of the Cole-Cole type with an α of about 0.4 (Namikawa 1975). The relaxation time spectra are reported to be fairly temperature independent (Taylor 1956, 1959). Semiconducting tungstate glasses also behave similarly. In molybdenum- and in vanadium-phosphate glasses, however, Mansingh and co-workers (1972, 1975, 1976) have shown that α has different values above and below the absorption peaks; for $\omega\tau \ll 1$, $\alpha = 0.6$ while for $\omega\tau \gg 1$, $\alpha = 0.4$. At very low temperatures, α tends to 0.9. A symmetric behaviour in $\log \epsilon''/\epsilon''_{\text{max}}$ vs $\log (\omega/\omega_{\text{max}})$ plots have been noticed by Hakim and Uhlmann (1971) who have discussed their results in terms of a distribution function suggested by Glarum.

Dielectric relaxation in borate and phosphate glasses have been studied by many

pure B_2O_3 glass does appear to exhibit feeble dielectric relaxation (figure 7) alkali borate glasses exhibit dielectric peaks around 25K at a frequency of 1 kHz (van Gemert 1977). The height of the loss peak is approximately proportional to the alkali concentration upto 20 mol % beyond which it decreases. This has been correlated with the fraction of tetrahedrally coordinated boron atoms and the relaxation may then be viewed as a consequence of the motion of the alkali ions among the four identical planes of the tetrahedron. The loss is generally characterized as a deformation loss, or, more appropriately as loss due to local motions. Activation energies for such motion are low

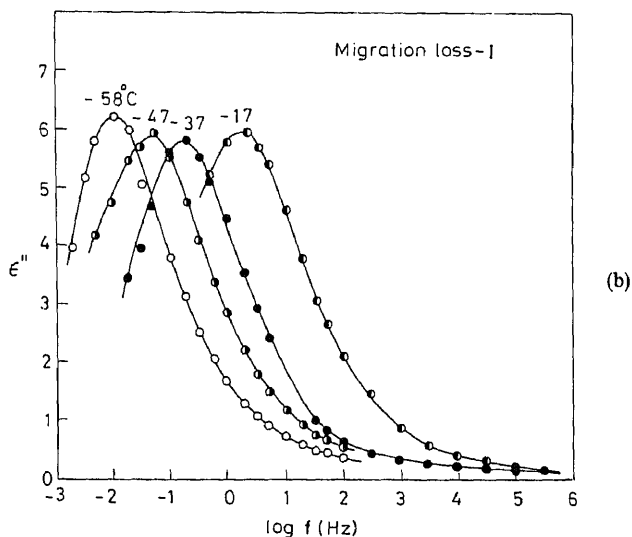
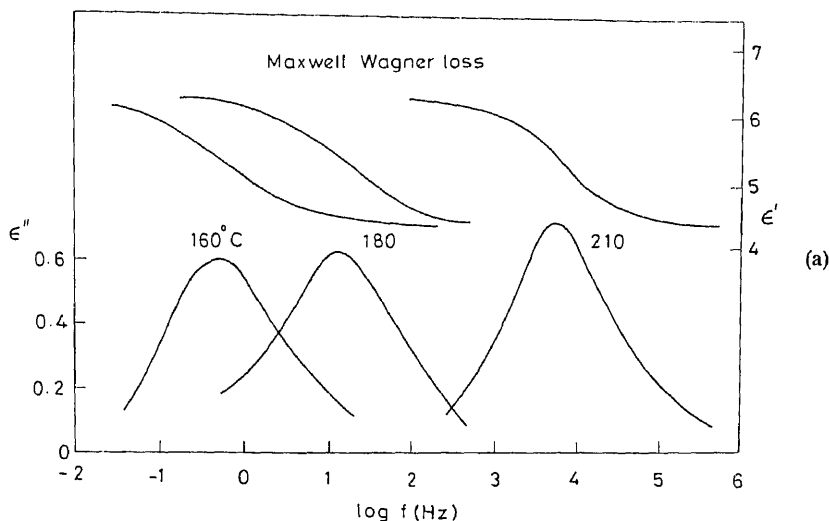


Figure 6. a, b.

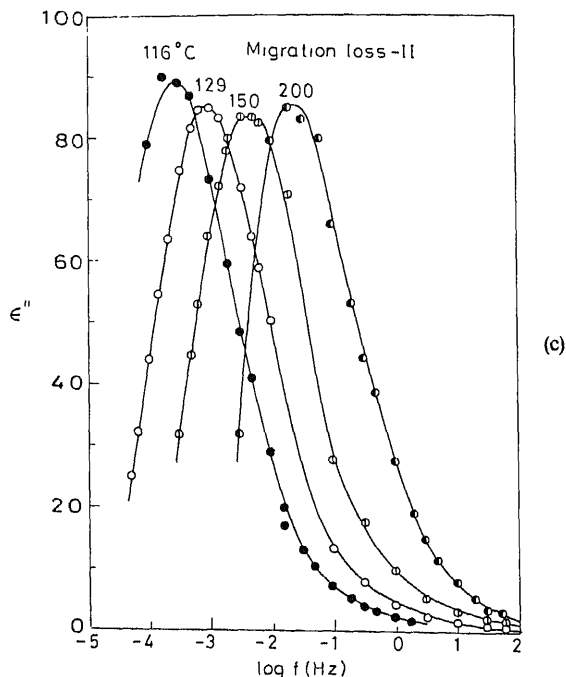


Figure 6. Typical dielectric relaxation based on (a) Maxwell-Wagner loss for an alkali borosilicate glass (b) migration loss (NLD) I for an alkali silicate glass (c) migration loss (NLD) II for an alkali silicate glass (after Namikawa 1975).

(ca 0.1 eV) (Stevens 1980). Similar losses due to local motion have been observed in silicates as well, where the activation barrier is ca 0.05–0.1 eV.

Dielectric relaxation studies of systems containing discrete anions are sparse. In their search for the so-called β -relaxations, Goldstein and co-workers (Johari and Goldstein 1970) found a loss peak at $\approx 0.16 T_g$ in a $\text{Ca}(\text{NO}_3)_2\text{-KNO}_3$ glass which, however, they did not regard as a β loss peak. At such low temperatures the β -relaxations are expected to be very diffuse. In this system as well as in the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ system (Johari and Goldstein 1970) one may expect that the actual β peak is swamped by the large d.c. conductivity (Hayler and Goldstein 1977). In sulphate glasses the dielectric loss peak was observed just below T_g at a frequency of 1 kHz (Rao 1980). β -relaxation peaks are generally believed to be universal features of the glassy state (Wong and Angell 1976; Goldstein 1969; Johari and Goldstein 1970, 1971; Hayler and Goldstein 1977) and are associated with ionic motion between wells separated by low barriers (0.1–0.4 eV). In fact, a.c. conductivity measurements in sulphate glasses corroborate the presence of short range motion characterized by such barriers which are clearly much smaller than

Table 2. Electrical properties of some ionically conducting glasses.

Molar composition	$\log \sigma_0^a$ ($\Omega^{-1} \text{ cm}^{-1}$)	$\Delta H_{\text{d.c.}}$ (kcal mol $^{-1}$)	$\log f_{\text{mo}}^b$ (Hz)	ΔH_{ac} (kcal mol $^{-1}$)	$\Delta \epsilon^c$	α^d	p^e
<i>Localized diffusion (LD)</i>							
1.2 Li ₂ O-28.2 B ₂ O ₃ -69.3 SiO ₂	1.3	34.3	12.7	25.6	1.8	0.3	1
7.5 Li ₂ O-92.5 SiO ₂	5.47	25.0	9.5	18.8	58	—	1
<i>Non-localized diffusion I (NLD I)</i>							
15 K ₂ O-85 SiO ₂	1.24	18.3	11.8	17.8	22	—	1.2
30 Na ₂ O-70 SiO ₂	1.92	14.5	12.5	14.0	17	—	1.4
30 Rb ₂ O-70 SiO ₂	1.80	15.0	12.5	14.7	16	—	1.0
30 Cs ₂ O-70 SiO ₂	1.18	16.0	11.5	15.7	17	—	3.2
<i>Non-localized diffusion II (NLD II)</i>							
15 Li ₂ O-15 K ₂ O-70 SiO ₂	2.78	25.6	12.4	26.2	96	0.4	9
8 Na ₂ O-12 K ₂ O-10 CaO-70 SiO ₂	2.56	26.4	11.2	26.1	317	0.4	10

^a σ_0 denotes the pre-exponential factor in the expression $\sigma = \sigma_0 \exp(-\Delta H_{\text{d.c.}}/kT)$, where $\Delta H_{\text{d.c.}}$ is the activation barrier; ^b f_{mo} is the pre-exponential factor in $f_m = f_{\text{mo}} \exp(-\Delta H_{\text{ac}}/kT)$ where ΔH_{ac} is an activation barrier to dielectric relaxation and f_m is the frequency at the loss maximum; ^c $\Delta \epsilon$ is the dielectric relaxation strength; ^d α is the Cole-Cole parameter; ^e p is a correlation factor.

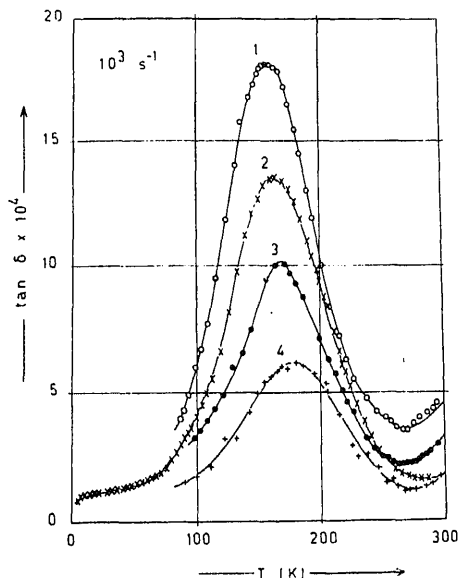


Figure 7. $\tan \delta$ versus temperature for B_2O_3 glass prepared from H_3BO_3 using different melting procedures: after heating at (1) 1000°C for 10 min (2) 1000°C for 30 min (3) 1000°C for 5 hr (4) 1200°C for 6 hr (after Quinten *et al* 1978).

Table 3. β -relaxations in some organic glasses.

Systems studied	T_g (K)	β -relaxation temperature, T_β , frequency	T_β/T_g
<i>Rigid molecules:</i>			
50 mol % <i>o</i> -fluorotoluene in <i>m</i> -fluorotoluene	121	Shoulder, 85K, 1 kHz	0.70
12 mol % chlorobenzene in <i>cis</i> -decalin	133	124K, 1 kHz	0.93
48.3 mol % 1-chloronaphthalene in tetrahydrofuran	111	112K, 500 Hz	1.0
38.1 mol % 1-chloronaphthalene in pyridine	147	103K, 1 kHz	0.7
<i>Alcohols:</i>			
2-Pentanol	133	104K, 10 kHz	0.78
3-Methyl-2-butanol	170	Shoulder, 150K, 10 kHz	0.88
<i>Non-rigid molecules:</i>			
Dimethyl phthalate	194	Shoulder, 175K, 1 kHz	0.90
Diethyl phthalate	184	157, 1 kHz	0.85
Isopropyl benzene	127	Shoulder, 115K, 1 kHz	0.91

consisting of clusters (regions characterized by a high degree of positional correlation) connected by tissue material of lower density within which particle motion is possible even below T_g (Goldstein 1975; Hayler and Goldstein 1979). Particle motion in such regions would then give rise to β loss peaks. It is worth noting that the cluster model has other significant implications in the phenomenology of the glassy state. Further.

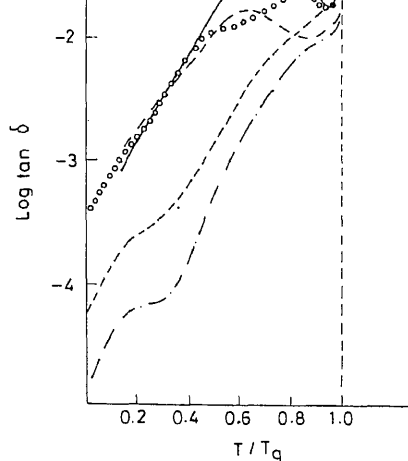


Figure 8. Variation of $\tan \delta$ with T/T_g for a number of molecular glass systems: chlorobenzene in *cis*-decalin (---) (1 kHz); mixture of *o*- and *m*-fluorotoluene (---) (1 kHz); 1-chloronaphthalene in tetrahydrofuran (O) (0.5 kHz); bromobenzene in tetrahydrofuran (— — —) (1 kHz); 1-chloronaphthalene in pyridine (——) (1 kHz). β -relaxations are clearly seen; low temperature anomalies are also evident in some cases (after Hayler and Goldstein 1977).

temperatures particularly when these ions are asymmetrically shaped. Investigations of anion motions and consequent dielectric loss behaviour in glasses, however, do not appear to have been reported.

3.2 The mixed alkali effect

'Mixed alkali effect' is the term used to describe non-linearities in the various properties of glasses with respect to composition containing more than a single-type of alkali ion (Isard 1969). Such deviations from linearity are particularly noticeable in properties connected directly with alkali ion motion (Isard 1969; Day 1974; Rao 1982). In dielectric loss measurements, for instance, the mixed alkali effect produces a pronounced dip in $\tan \delta$ (Stevens 1951; Kostanyan 1960; van Ass and Stevens 1974a, b; van Gemert *et al* 1974; Sundar and Rao 1982a) and a characteristic loss peak in internal friction measurements (Zdaniewski *et al* 1979). In d.c. conductivity the mixed alkali effect gives rise to a clear minimum (Bartholomew 1973; Rao and Sundar 1980; Sundar and Rao 1982b) and to substantial alterations in alkali ion diffusivities (Terai 1971; Ohta 1975; Fleming and Day 1972) in a host of glasses; in other properties (*e.g.* molar volume), though, the mixed alkali effect is rather slight (Ivanov 1964; Caporali 1964). Figure 9 shows the mixed alkali effect as manifested in the various properties related to ionic motion in a range of glasses. The effect has been seen in both network (Day 1974) and discrete anion glasses (Rao 1982; Rao and Sundar 1980; Sundar and Rao 1982a). It can also be observed as a 'mixed anion effect' so that currently, it is often referred to as the 'mixed' ion effect'.

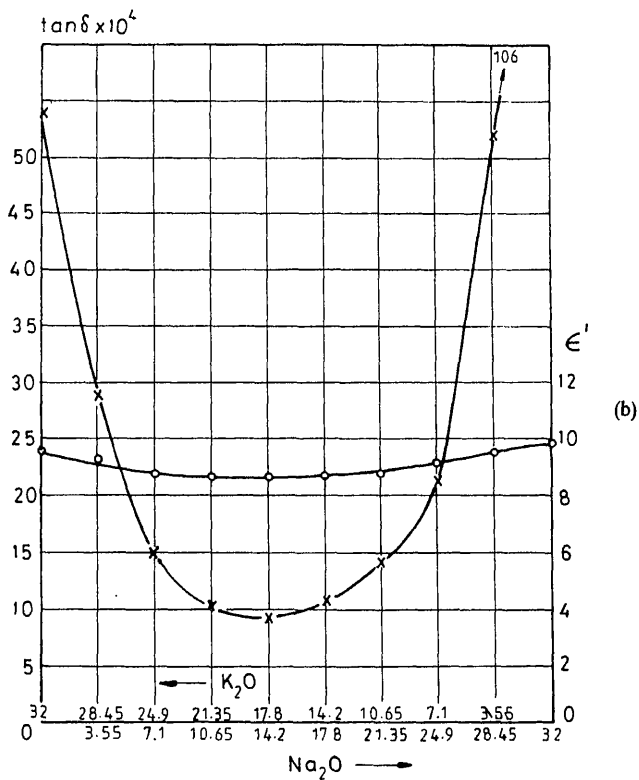
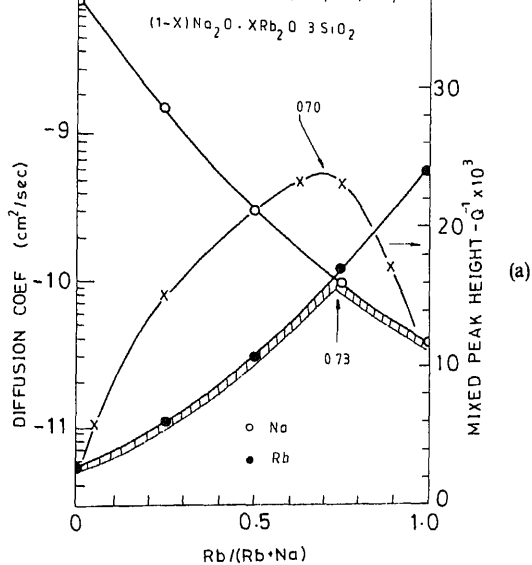


Figure 9

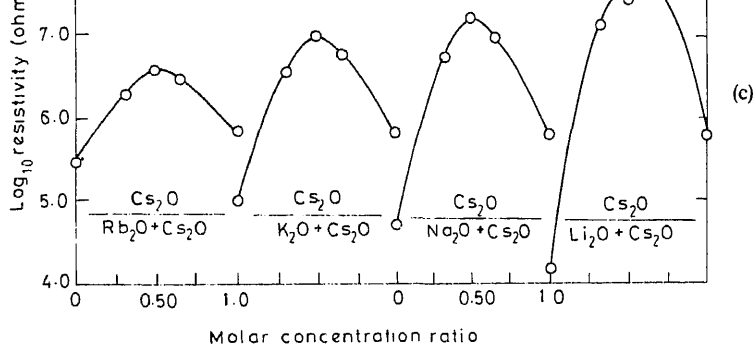


Figure 9. (a) Alkali diffusion coefficients and the mixed alkali internal friction peak as a function of composition in a mixed-alkali silicate glass. Cross hatch denotes the slower ion; (b) variation of $\tan \delta$ and ϵ' with composition in a mixed-alkali lead oxide-calcium fluoride-silica glass; (c) variation of resistivity with composition for various mixed-alkali silicate glasses (after Day 1976).

Many theoretical approaches have been made to explain the mixed alkali effect. These can be grouped under three heads *viz.* (a) structural (Stevels 1957; Charles 1965), (b) electrodynamic (Hendrickson and Bray 1972a, b) and (c) thermodynamic theories (van Gemert and Stevels 1978). Structural theories stress the importance of void sizes necessary for the transport of ions and consider the possibility of a blocking effect which reduces the effective mobility of the ions. In the electrodynamic theories the dissimilar masses of the ions (which give rise to dissimilar vibrational frequencies) develop an interaction energy due to the electrical fields of the vibrating ions. This energy affects the activation barrier and hence the motion of the ions. The thermodynamic theories consider that the simultaneous presence of ions of different sizes affects the total interaction energy and hence the migration barrier. Phase separation (Charles 1965), increase of pairing energies (Sakurai and Ooka 1968), anharmonicity of thermal vibrations (Weyl and Marboe 1962) and micro-strain fields (Rao and Sundar 1980) have all been considered as possible origins of the mixed alkali effect but, to date, no single model has proved to be either universal or quantitatively accurate in accounting for this motion dependent phenomenon.

The decrease in values of $\tan \delta$ in mixed alkali regions suggests two possibilities: (i) the ions stabilize in their own positions in response to the polarizing field or (ii) the consolidated motion of these ions in a sufficiently small region does not involve changes in polarization. As we shall see a little later, the latter possibility is consistent with the results of internal friction measurements.

3.3 Mechanical relaxation

Mechanical relaxation is measured using different techniques in different frequency ranges. Between 0.1 and 250 Hz it is measured by following the torsional oscillations of

Single component network glasses such as SiO_2 , B_2O_3 (Kurkjian and Krause 1968) and others exhibit very low energy losses. The losses are generally attributed to the network oxygen response and sometimes to the very small concentrations of impurities such as water. Ballaro *et al* (1975) for example, have observed a low temperature internal friction peak in silica glass with an activation energy of 0.05 eV in the megahertz region (figure 10). Binary alkali silicates have been the most extensively investigated and these, in general, exhibit two internal friction peaks (at ~ 1 Hz); one between 233 and 248 K (Forry 1957; Ryder and Rindone 1960, 1961; Zdaniewski *et al* 1979) and the other between 373 and 573 K (Ryder and Rindone 1960, 1961; Shelby and Day 1969, 1970). The low temperature loss peak is believed to be due to alkali ion motion (generally referred to as the single alkali peak) since it has an activation energy (0.7–1.0 eV) very similar to that observed for d.c. conductivity in a number of glasses (Higgins *et al* 1972). The position of the second peak is dependent upon the nature of the modifying cation, silica content, traces of dissolved water etc., so that it is of uncertain origin. It has also been attributed to non-bridging oxygen ions (Rotger 1958), possibly because its magnitude has generally been found to be proportional to the alkali content (Forry 1957; Mohyuddin and Douglas 1960; Douglas 1963).

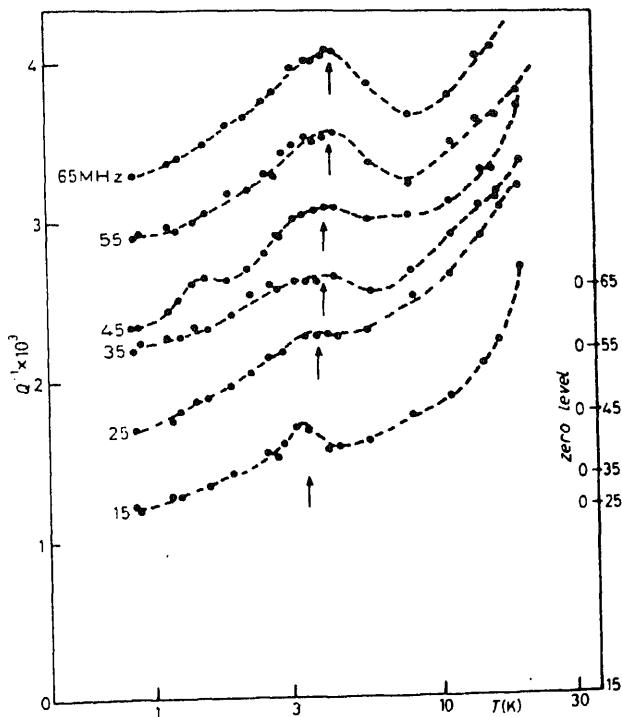


Figure 10. Internal friction coefficient as a function of temperature for SiO_2 glass at the frequencies shown. The ordinate scale for each frequency has been shifted upwards (scale on the RHS) (after Ballaro *et al* 1976).

The mixed alkali effect is very sensitively detected in internal friction experiments through the so-called 'mixed alkali peak' which appears (at ≈ 1 Hz) at a temperature slightly greater than that of the single alkali peak (Rotger 1941; Jagdt 1960). Increasing concentration of the second alkali the mixed alkali peak shifts to higher temperatures and its magnitude is also increased. Concurrently, the single alkali peak shifts to higher temperatures so much so that when the proportions of the two alkalis are comparable only a single, giant loss peak is observed (Zdaniewski *et al* 1972). They have pointed out earlier that the origin of mixed alkali relaxation is not very clear. In the dielectric loss it attains a minimum whereas a giant loss peak appears in internal friction it appears that the elastic dipole (formed from dissimilar alkali ions) is somehow rearranged in the a.c. stress field without causing alterations in electric polarization. One is tempted to think that such a possibility ensues primarily from the rather high values of time constants in internal friction measurements as compared with the time scale of polarization renormalization.

Internal friction losses have also been noted at very high frequencies (megacycle region) in glassy selenium and GeS_2 (Carini *et al* 1978). An absorption minimum has been noted for these materials at 150 K and 450 K respectively which the authors have discussed in the light of a 'stochastic resonance absorption' model. Mechanical relaxations of a variety of metallic glasses have also been investigated. Tyagi and co-workers (1979) have measured the internal friction of $\text{Fe}_{24}\text{Ni}_{40}\text{P}_{14}\text{B}_6$, $\text{Fe}_{29}\text{Ni}_{49}\text{B}_6\text{Si}_2\text{P}_4$ and $\text{Fe}_{80}\text{B}_{20}$ glasses at frequencies of 0.2 and 1 Hz. The increase in internal friction with temperature yields an activation energy of $40\text{--}80\text{ kcal mol}^{-1}$ which the authors attribute to unspecified atomic motions.

Ultrasonic studies of glasses, particularly silica (Golding *et al* 1973; Hunklinger *et al* 1972) and some chalcogenides (Ng and Sladek 1975; Farley and Saunders 1977) have revealed an anomalous saturation of the ultrasonic attenuation at very low temperatures. Many other physical properties, such as heat capacity (Fisler *et al* 1966) also behave anomalously in this temperature range. Theoretical approaches to the problem were first made by Anderson and Bommel (1955) and later by Anderson *et al* (1967). It seems that these anomalous features may be explained if we assume the existence of two-state potential wells separated by low energy barriers (asymmetric double-well potential) (Phillips 1972). Particle motion between these wells can occur either by tunnelling through or by hopping over the barrier. The model is sufficiently general that it can be used to account for various anomalies through an imaginative interpretation of structural data. Indeed, the low temperature anomalies in fused quartz have been attributed by Anderson and Bommel (1955) to the displacement of SiO_4 tetrahedra which is consistent with the random network model proposed for these glasses. In borosilicate glasses too, studies by Arnold *et al* (1974) have indicated the presence of such anomalies. Currently, it is believed that such anomalies are a fundamental property of glasses and attempts have been made to correlate the glass transition temperature with the density of such energy-split states (Raychaudhuri and Pollack 1981; Cohen and Grest 1981).

3.4 The glass transition and associated relaxations

We have pointed out earlier that pronounced dielectric loss occurs near the glass transition. Very similarly internal friction studies also show loss peaks which are

transition as it occurs upon supercooling of liquids is even more informative. The glass transition then corresponds to the kinetic 'freezing' or the falling out of equilibrium, of the metastable supercooled liquid. It is at once obvious that the 'freezing' is a time dependent phenomenon which logically leads to the postulation of a 'fictive temperature' (Hagy and Ritland 1957; Haddad and Goldstein 1978). This is a structure related temperature and can be regarded as that temperature where the structure of the glass is, in fact, its equilibrium structure. Consequently, the fictive temperature of a glass and the relaxations around T_g are related to each other. When a glass is brought rapidly to a temperature above the fictive temperature it relaxes to the equilibrium structure with a characteristic relaxation time spectrum. Many experiments have been designed to follow the relaxations at T_g including measurements of refractive index (Macedo and Napolitano 1967), density (Ritland 1954), thermal expansivities (Hagy and Ritland 1957; Williams and Angell 1973) and heat capacities (Boehm *et al* 1981). In general, the relaxation time may be related to the fictive temperature as (Narayanaswamy 1971),

$$\tau = A \exp [(x\Delta h/RT + (1-x)\Delta h/RT_f)], \quad (54)$$

where a , x and Δh are constants and T_f is the fictive temperature. It is clear that as T tends to T_f , τ has essentially an Arrhenius dependence which corresponds to small displacements from equilibrium. The relaxation in this region is generally described as non-linear response (Wong and Angell 1976) and we do not propose to discuss it further in this article. However, we give below a summary of our understanding of the kinds of motion that characterize T_g mostly for purposes of completeness.

Relaxation times become very large as a supercooled liquid approaches T_g . Since cooling leads to a considerable decrease in volume and entropy, configurational rearrangements that take place near T_g become increasingly difficult and more cooperative (Barlow *et al* 1966; Rao 1979). Over a substantial range of temperature, transport properties of the supercooled liquid are non-Arrhenius and may be represented by the well-known Doolittle (1951) or Vogel-Tammann-Fulcher (VTF) (Vogel 1921; Tammann and Hesse 1926; Fulcher 1925) equation,

$$\phi = \phi_0 \exp [\pm B/(T-T_0)] \quad (55)$$

where ϕ is the transport property being measured and B is usually an activation barrier and T_0 a constant with units of temperature. Most theories of the glass transition have addressed themselves to an explanation of such a temperature dependence and to an identification of T_0 with a truly thermodynamic glass transition temperature (Kauzmann 1948; Rao 1979). The experimental glass transition, however, occurs beyond T_0 and corresponds to the 'freezing-in' of excess quantities such as entropy or free volume. The non-linear relaxations alluded to above are associated with these frozen-in excess quantities (Wong and Angell 1976).

Considerable effort has also been expended in the literature on a discussion of the so-called 'order parameters' (Cooper 1977; Gupta and Moynihan 1976, 1978; Kovac 1981) which can be any of the excess quantities that determine the free energy of the liquid and hence the glass transition temperature. (It has been conventional to use the term 'order parameter' in phase transitions so that it denotes a perfectly ordered state when equal to

unity. The order parameter cooperatively vanishes at the transition temperature. In the context of the glass transition it is preferable to designate the excess quantities of a supercooled liquid as 'ordering parameters' after Cooper (1977)). It has been known for a long time (Davies and Jones 1953) that the Prigogine-Defay ratio, π , for the glass transition is either equal to or greater than unity depending upon whether a single ordering parameter or a multiplicity of ordering parameters govern the glass transition (π is defined as equal to $(\Delta\alpha)^2/TV\Delta C_p\Delta\beta$ where $\Delta\alpha$, ΔC_p and $\Delta\beta$ are changes in the expansivity, heat capacity and compressibility respectively at T_g). Further constraints upon ordering parameters that determine the value of π have been investigated by several workers (Kovac 1981; Gupta and Moynihan 1976).

A model of the glass transition that is particularly attractive in the context of relaxations has recently been discussed by Perez *et al* (1981). Their approach is based on Goldstein's model (Goldstein 1975; Hayler and Goldstein 1977) which considers glass as consisting of dense clusters embedded in a connective tissue of low density. Particle motion is then considered to occur within the tissue material and across cluster boundaries. From an elaborate consideration of relaxation time spectra and internal friction losses as a function of temperature Perez *et al* (1981) have attributed the β loss peaks to cooperative rearrangements in the tissue material and α relaxation to thermally activated particle motion on cluster surfaces.

3.5 Magnetic resonance spectroscopy

Studies which have used magnetic resonance spectroscopy to understand particle motion in the glassy state are relatively few in number. Even these investigations are concentrated, specifically, either on ionic motion *per se* or on the anomalous behaviour of T_1 (the spin-lattice relaxation time, discussed in §2.4) due to the two-level system (TLS).

The work of Bray and co-workers on NMR studies of ionic motion in glass has been truly monumental. In silicate and borate glasses, for example, Hendrickson and Bray (1974) have used ^7Li NMR to explore the behaviour of the spin-lattice relaxation time. A semilog plot of inverse corrected linewidth *vs* $1/T$ (figure 11) obtained in $\text{Li}_2\text{O} \cdot \text{SiO}_2$ glass clearly shows the presence of motional narrowing which has been analysed in terms of equation (50). Three straight line segments (denoted by I, II and III) are evident in the plot with region II having the highest slope and, consequently, exhibiting the highest activation energy. Region I has been attributed by the authors to short range motion which has a smaller activation energy and higher values (10^{-1} to 10^{-4} kHz) of B , as in (50). In region II the activation energy is about 0.6–0.7 eV and the B value is much smaller ($\sim 10^{-12}$ kHz); the latter feature has prompted the authors to assign this region with predominantly long range motion of the alkali ion. It is interesting to note that motional narrowing in the glassy region indicates two distinct regimes of ionic motion. There is a close correspondence between these results and the dielectric relaxation discussed earlier. Hendrickson and Bray (1974) have found

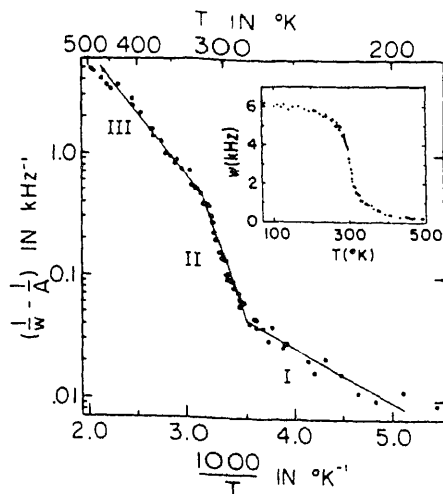


Figure 11. A plot of log inverse corrected ^7Li linewidth vs $10^3/T$ for $\text{Li}_2\text{O}-2\text{SiO}_2$ glass. Inset: the measured linewidth as a function of temperature, which clearly shows motional narrowing (after Hendrickson and Bray 1974).

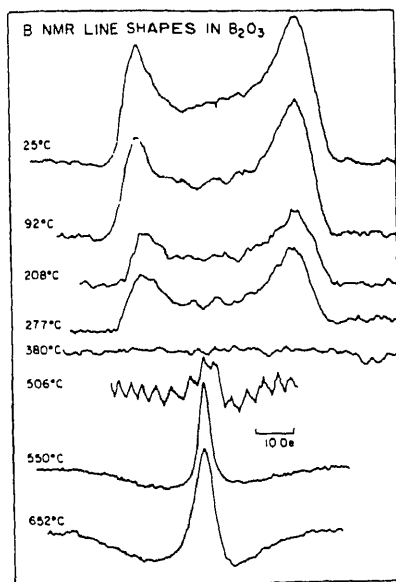
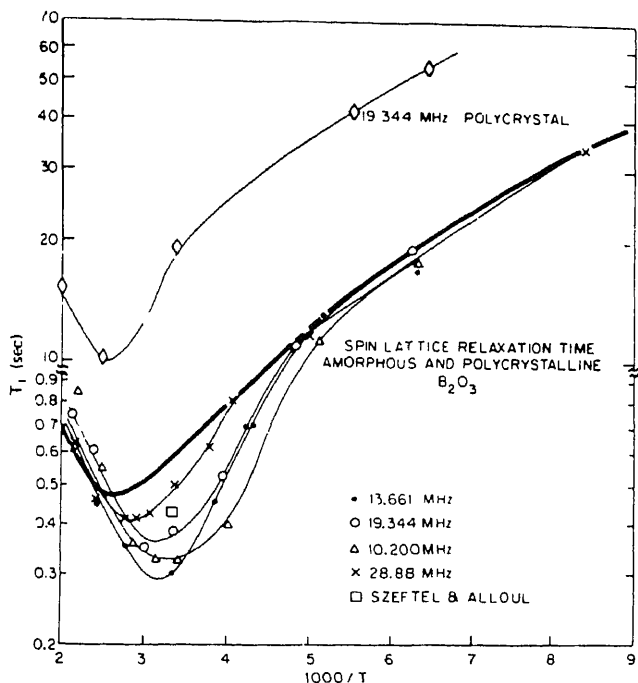


Figure 12. Changes in the ^{11}B NMR spectrum in amorphous B_2O_3 as a function of temperature (after Rubinstein 1976).

25°K above the glass transition. The author suggests that the structures of the two glasses are very similar but that B_2S_3 behaves as a molecular fluid beyond T_g .

Rubinstein and Resing (1976) have also reported NMR studies which are related to TLS in glassy as well as in polycrystalline B_2O_3 . An anomalous low minimum has been observed in T_1 which is mildly frequency dependent. From figure 13 which shows T_1 as a function of temperature for both the crystal and the glass, it becomes clear that relaxation is ≈ 30 times faster in the glass than in the crystal. The authors have analyzed their observations in terms of asymmetric double-well potentials which were earlier used to rationalise the existence of low temperature thermal anomalies. Figure 13 also shows a minimum in T_1 and this has been discussed in terms of temperature dependent broadening of the phonon spectrum which, in turn, causes a decrease in the effective density of states. Szeftel and Alloul (1978) have studied nuclear magnetic relaxation in Se, B_2O_3 , borate and borosilicate glasses using ^{77}Se , ^{11}B , ^{23}Na and ^{29}Si NMR in very low temperature region. These workers have observed that T_1 is field independent and that it has a complicated temperature dependence of $1/[T^{(1+\gamma)}]$ where $0 \leq \gamma \leq 1$. They have also confirmed the presence of T_1 minimum in B_2O_3 at 300 K but most importantly they attribute the relaxation time behaviour to an electric field fluctuation at the nuclear site due to the tunnelling of nearest neighbour defects. These defects have tentatively been identified as bridging oxygens tunnelling between a pair of potential wells.

Muller-Warmuth and Otte (1980) have recently reported a study of nuclear magnetic spin relaxation in a number of organic compounds. In an investigation of solutions of



benzene and substituted benzenes in glass forming solvents such as o-terphenyl, 1,2-decalin and benzophenone, they found a minimum in T_1 around 100 K. Such an anomalous decrease in T_1 has been analysed in terms of distribution of correlation times and has been attributed to the characteristic low-lying excitations present in amorphous systems. The activation energy of such correlation times was found to be generally very low (≈ 0.1 eV).

Motional narrowing can play an equally significant role in ESR spectroscopy as is evident from a recent study by Antsiferova *et al* (1973) of an organic free radical (PADS) in supercooled aqueous glycerol. They have compared simulated line-shapes obtained using various models with experimental results and have concluded that the jump diffusion model (§3.5) is more appropriate to a viscous medium than the Brownian motion model. It is quite curious that ESR studies have not so far been widely used to study particle motion in the vitreous state. Some work in this direction has recently been initiated in our laboratory (Parthasarathy *et al* 1981a) both in organic and in inorganic glasses primarily to gather information on particle motion in the neighbourhood of T_g . Such data, it was felt, would be vital to an understanding of the glass transition itself. It must, however, be emphasized that analysis of all the dynamical features associated with the non-linear relaxation region through ESR relaxation times is avowedly difficult. The variation of relaxation time *per se* with temperature should nonetheless reveal the evolution of liquid-like behaviour within the glass.

Experiments on organic glasses were made using an ESR spin-probe, TEMPONE (2,2,6,6-tetramethyl-piperidin-4-one-1-oxyl) which was dissolved in the liquid under study at a concentration of $\approx 10^{18}$ spins cm^{-3} . Transverse correlation times of this probe were then studied through the glass transition. The spectra of TEMPONE in glycerol and in methyl salicylate are shown in figure 14a, b. Correlation times, τ_c , were obtained using

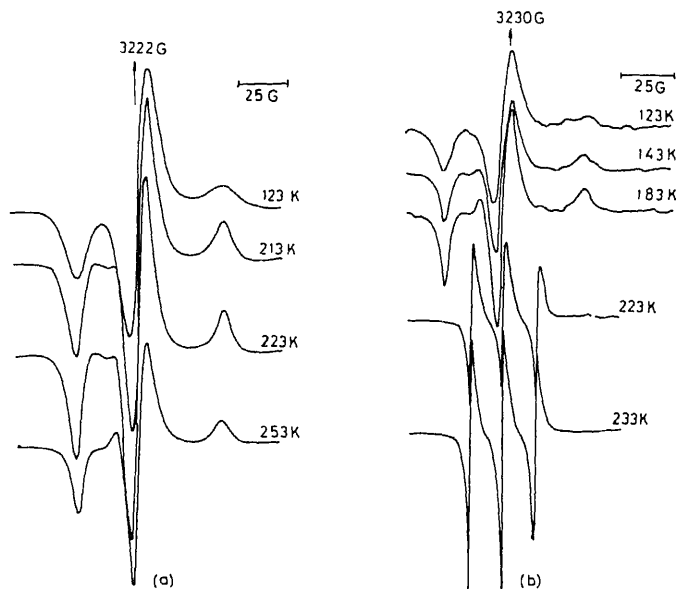


Figure 14. ESR spectra of TEMPONE in (a) glycerol and (b) methyl salicylate at selected temperatures (after Parthasarathy *et al* 1981).

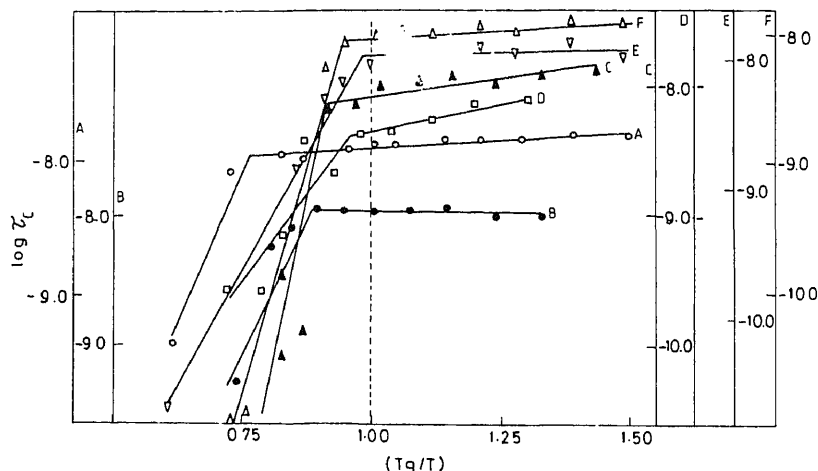


Figure 15. A plot of $\log \tau_c$ against T_g/T for A: glycerol; B: *o*-toluidine; C: methyl salicylate; D: propylene carbonate; E: dimethyl phthalate; F: *p*-anisaldehyde. The broken line indicates T_g (after Parthasarathy *et al* 1981).

the procedure of McConnell (Stone *et al* 1965) and the variation of $\log \tau_c$ with T_g/T is shown in figure 15 for all the liquids studied. It is clear that upto a temperature T_k , where $T_k \geq T_g$, τ_c is rather large and generally independent of temperature. In the supercooled region where $T > T_k$, τ_c decreases rapidly. The authors have rationalised their observations using the cluster model of glass, elements of which were discussed earlier in this section. In this model, the glass transition may be considered to correspond to a 'congelation' of clusters as the melt is cooled. The existence of a considerable amount of less dense, intercluster tissue material is, of course, assumed. The TEMPONE radicals being themselves heterogenities were considered to act as nuclei which eventually grow into clusters upon cooling. It is for this reason that their correlation times were seen to increase rapidly in the supercooled region and reach values characteristic of the glass well above T_g (at T_k). It is quite likely that the extent of hydrogen bonding is at least partially responsible for the deviation of T_k from T_g and, hence, for the different values of T_k observed in the various glasses. The activation energy obtained from the supercooled region ranged from 0.6 to 3 eV.

In inorganic glasses, transition metal ions may be effectively used as spin probes. The large relaxation times of Mn^{2+} and Fe^{3+} have been exploited in a study of the glass transition in 3 glasses: a discrete anion sulphate glass, a covalent network phosphate glass and a complex PbO-PbCl_2 glass of intermediate ionicity (Parthasarathy *et al* 1981b). Surprisingly, it was found that the line widths were constant through the glass transition, showing thereby no motional narrowing effects (figure 16). One wonders whether motional narrowing was offset by line broadening mechanisms operating in glasses with relatively high T_g 's or whether such narrowing takes place in the supercooled liquid at temperatures which were not accessible to these workers.

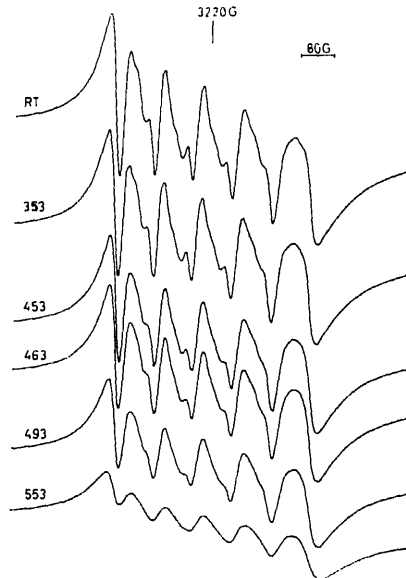


Figure 16. Variation of the ESR spectrum of Mn^{2+} in a sulphate glass ($T_g \simeq 460$ K) at selected temperatures (after Parthasarathy *et al* 1982).

3.6 Vibrational spectroscopy

The discussion in §2.3 indicated the possibility of using vibrational spectroscopy very effectively to understand particle motion in the glassy state. Little, however, appears to have been accomplished in this direction (Angell 1980). Rothschild (1974) has recently analysed the 1033 cm^{-1} ring deformation band in quinoline in the crystalline, liquid and glassy states. He has found that relaxation in this molecule is primarily vibrational. Relaxation times appear to be much higher in the crystalline rather than in the glassy state where the wide distribution of environments may promote effective relaxation.

Reports of other recent vibrational band shape studies in viscous liquids and glasses has been reviewed by Angell (1980). Raman studies of organic (toluene) and inorganic ($\text{KNO}_3\text{-Ca(NO}_3)_2$) glasses have been reported (Clarke and Miller 1972). While very little heterogeneous band broadening has been found above T_g in the case of toluene, band broadening appears to be substantial in the case of the nitrate glass.

The behaviour of IR band shapes has been investigated in a sulphate glass (Sundar *et al* 1982) in order to understand particle motions around T_g , using the 620 cm^{-1} sulphate deformation mode. Surprisingly, the band-width was found to increase upto T_g and thereafter, it remained constant. Correlation times, were obtained using the Fourier methods discussed in §2.3, and these are shown as a function of T/T_g for a number of compositions in figure 17. Second moments were also evaluated using (38b) and it was found that these reached saturation values just below T_g in all the compositions. The kind of saturation behaviour observed both in τ_c and second moments appears to indicate that liquid-like particle motion evolves in glasses at temperatures less than T_g . This would indeed be quite consistent with a cluster model of

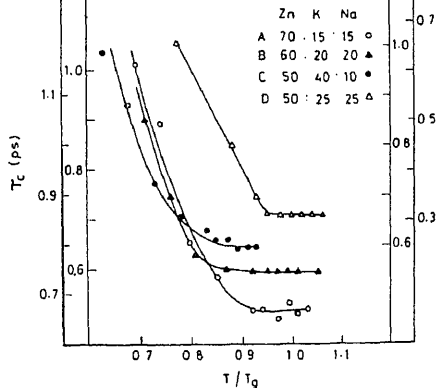


Figure 17. A plot of τ_c , obtained from IR band-shape analysis, as a function of T/T_g for sulphate glasses whose molar compositions are as shown (after Sundar *et al* 1982).

3.7 Mossbauer studies

A number of interesting Mossbauer studies, particularly through the glass transition, have been reported in the literature. One of the earlier studies is by Cooper and co-workers (Gosselin *et al* 1968) who studied the Mossbauer spectra of a sodium trisilicate glass containing 8.25 wt % of Fe_2O_3 through the T_g . They have reported that the line width of the Fe^{2+} resonance is unchanged while that of Fe^{3+} broadened. Recoil-free fraction, isomer shift (is) and quadrupole splitting (qs) were observed to decrease with increase in temperature. More recent studies have confirmed that changes in these parameters, *viz.*, recoil-free fraction, Lamb-Mossbauer factor, line-width, is and qs through the glass transition are, in fact, quite generally found (Champeney 1979). Figure 18 shows the general behaviour of recoil-free fraction as a function of temperature for both glassy and crystalline states.

In their studies of Fe^{2+} ions in glycerol, Abras and Mullen (1972) have found evidence for the broadening occurring both due to jump and continuous diffusion of particles depending upon temperature. A more recent report on x-ray attenuation and Mossbauer line broadening in an aqueous phosphoric acid solution of Fe^{2+} , however, presents evidence against the jump model (Ruby *et al* 1975). Barnes and Langevin (1963) have investigated a frozen aqueous solution (FAS) of an ion salt and have noted that the recoil-free fraction decreases continuously with temperature and vanished at T_g (210 K). Brunot *et al* (1971a, b) also report similar findings in their FAS studies. The decrease in recoil-free fraction at the T_g has also been recorded by Simopoulos *et al* (1970). Yet another recent report of the Mossbauer study of ferrocene in *o*-terphenyl (Vasquez and Flinn 1980) notes that while $\langle x^2 \rangle$ decreases at T_g , line-broadening is not significant at temperatures just greater than T_g (figure 19). A significant point made by these workers is that values of the glass transition temperature obtained through studies of transport properties such as diffusion and viscosity should be distinguished from those obtained from static properties such as specific volume, enthalpy or power spectrum.

A qualitatively different approach to the problem has been adopted by Ruby and co-workers in their reports of Mossbauer studies on ferrocene in butyl phthalate (Flinn *et*

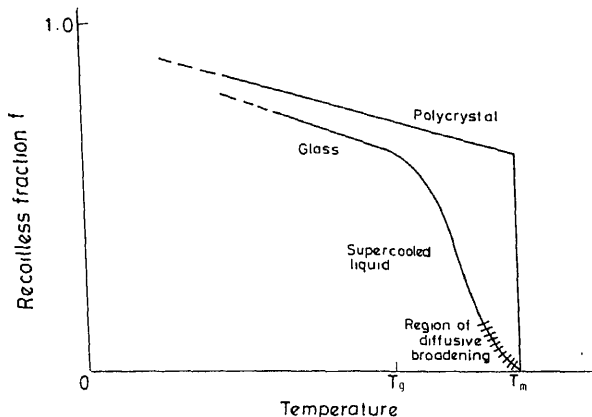


Figure 18. A schematic diagram of the variation of the recoil free fraction as a function of temperatures. It may be noted that diffusive broadening in glasses takes place well beyond T_g (after Champeney 1979).

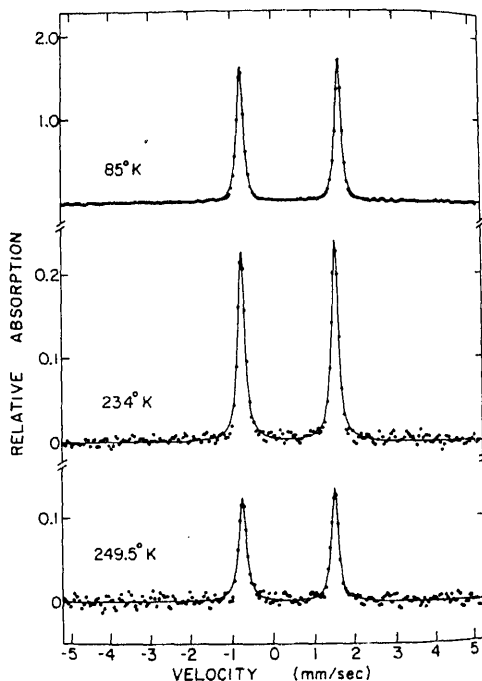


Figure 19. Mossbauer spectra of ferrocene in *o*-terphenyl for selected temperatures. While the recoil free fraction decreases rapidly beyond the T_g , it is significant that the line width shows no clear-cut increase (see figure 18) (after Vasquez and Flinn 1980).

al 1976; Ruby *et al* 1976) and phosphoric acid. They have observed an increase in $\langle x^2 \rangle$ beyond T_g but they note that rotational relaxation is unlikely to be observed in

decrease in elastic scattering intensity in terms of 'soft modes' as interpreted in the context of glasses. As Flinn *et al* (1976) remark, 'It is not that (such) transverse modes of the liquid gradually disappear with decreasing viscosity, but they are shifted to lower energies'. Considering the exciting possibilities that such an approach opens up and the fundamental importance of soft modes themselves, we feel that a brief digression into the soft mode postulate will not be out of place here.

The concept of soft modes as a basis for understanding phase transitions in solids has been developed over the last two decades and has provided a unifying structural approach to phase transformations (Rao and Rao 1978). The softening of vibrational modes or of elastic stiffness constants, it may be noted, has long been recognized as the origin of lattice instability (Born and Huang 1954). In the present context, the applicability of the notion of phonons to disordered solids has been discussed by several authors and has been excellently summarized by Wong and Angell (1976). It is well known that the glass transition corresponds to the onset of the loss of solid-like behaviour as the vitreous solid undergoes transition. Against this background, therefore, it is attractive to consider that the decrease in force constants of some phonon modes at the glass transition, gives rise to large amplitude motion of particles which is, essentially, the feature of a soft mode. Unlike solid-solid transformations, no new vibrational modes may be expected to appear at the T_g , which would strengthen and stabilize the glassy phase. It is also worthwhile to note that there may not be complete softening of all modes at T_g since the properties of the vitreous state are characterized by distributed relaxations. In this context, it is likely that long- and short-range phonons in glasses are also governed by a distribution of force constants which may not completely soften. Thus, the soft mode that may drive a glass transition is quite likely to be different in its details from the soft mode that drives crystalline transitions, a point made by Flinn *et al* (1976). The advantage in the soft-mode approach is that it provides a structural method of describing the glass transition as it occurs in the *glass*; theories that describe this transition from the standpoint of the supercooled liquid are, in contrast, essentially theories of viscosity in which the glass transition marks the termination of the liquid regime.

To sum up, we note that the increase in amplitude of the transverse modes, $\langle u^2 \rangle$, seen in Mossbauer experiments is significant in that it suggests the possibility of developing an entirely new approach to the problem of the glass transition in glasses.

4. Computer simulation and particle motion

At the outset we note that computer simulation studies reported in the literature have concentrated upon elucidating particle motions in the neighbourhood of the glass transition (Frenkel and McTague 1980; Angell *et al* 1981). There appears to have been no study that has sought to describe either the TLS or, indeed, the other types of motion in the glassy state described earlier. However, computer simulation studies in supercooled regions which have been performed with realistic potentials have brought out some of the most significant features related to the glassy state. Both Monte Carlo (MC) (Raveche 1976; Raveche and Streett 1976; Wendt and Abraham 1978; Angell 1980) and molecular dynamics (MD) (Kristensen 1976; Rahman *et al* 1976; McTague *et al* 1978; Clarke 1979) techniques may, in principle, be employed but the latter is

autocorrelation effects. In this section we summarize some of the recent computer simulation studies which, in our opinion, enable us to understand particle motion in the glass transition at a fundamental level.

In a recent article, Angell *et al* (1981) have reviewed computer simulation experiments to explore the effect of the (assumed) inter-particle potential upon glass formation. It is now well-known that computer simulation studies entail the use of very high rates of quenching ($\approx 10^{12}$ deg K sec $^{-1}$) (Angell 1982) and of a number of particles that usually does not exceed a few thousands (≈ 4000) (Cape and Woodcock 1979). Consequently, several features of the simulated glass transition do not completely match those of a 'real' glass transition. In these studies, the T_g itself is located through the behaviour of the diffusion coefficient (Angell *et al* 1981). In simple fluids, it has been found that diffusivity approaches zero at T_g more rapidly than is the case with related laboratory glasses. Further, diffusivity in a real glass can be quite low (10^{-18} cm 2 sec $^{-1}$) but in a simulated glass it is often more than 10^{-5} cm 2 sec $^{-1}$. This can be simply understood from the fact that in many simple polar molecules the product of $\tau_D D$ is a constant ($\approx 2 \times 10^{-16}$ cm 2) which for a diffusivity of 10^{-18} cm 2 sec $^{-1}$ would give rise to relaxation times of ≈ 100 sec, the time-scale of laboratory experimental measurement. In the case of a simulated glass T_g would occur even at a diffusivity of roughly 10^{-6} cm 2 sec $^{-1}$, because the corresponding relaxation time would be $\approx 10^{-10}$ sec which is still roughly 100 times the simulated cooling rate. In such a short time the system can only relax vibrationally and not configurationally. It has also been noted (Damgaard-Kristensen 1976) that a simulated glass transition is rather smeared-out and that the density of a simulated glass is $\approx 7\%$ lower than that of comparable laboratory time-scale glasses. A more disturbing feature of these studies is the size dependence of the approach to equilibrium (Clarke 1979) which hints at the possibility that most reported measurements may not correspond to well-relaxed systems. The significant results of simulation studies are as follows. (a) They affirm that glass formation can, indeed, ensue from supercooling of the melt. (b) Glass formation appears to be controlled by the repulsive part of the potential: the softer the potential, the lower is the glass-forming tendency (Alder and Wainright 1960; Raveche 1976; Hoover *et al* 1971; Hiwatari 1978). This finding seems to accord very well with the fact that the alkali metals, which are described by soft potentials have, as yet, not been vitrified, in contrast to transition metals which have harder potentials and have been vitrified (Chen 1980). (d) Relaxational behaviour also appears to be controlled by the softness of the potential (Clarke 1979; Woodcock 1976, 1978; Barker *et al* 1975). Different types of potentials have been used in several reported studies and interesting results with respect to the structure of glasses so formed have been obtained. From the foregoing it is quite clear that the choice of an interaction potential has a profound influence both on the local structures in the simulated glasses and upon their relaxational behaviour.

5. Concluding remarks

In the foregoing sections we have discussed several approaches to the study of particle motions in glass that principally involve spectroscopic techniques. Other methods are indeed available: for instance, neutron scattering, that has been used with particular

studies. Our choice has been directed by considerations of relevance of the techniques to a large variety of glasses and of directness of the information obtained. We feel that the techniques discussed above meet such criteria to a greater extent than others, though this is debatable.

In the discussion of dielectric and mechanical relaxations, we have found that both variable temperature and variable frequency approaches have been used, and that the power absorbed from the imposed field is used for particle motion. Informally, these techniques may consequently be directly related to jump frequencies and to associated relaxation times. In resonance spectroscopy, on the other hand, information with respect to particle motion can be obtained only through perturbations caused by the absorption or emission band characteristics. These spectroscopic techniques are nonetheless elegant, the mathematical apparatus available for data-analysis is powerful, and data may be obtained about the particles whose motion is being studied. However, these techniques, particularly vibrational spectroscopy, are comparatively rarely utilised in the context of the study of particle motion in glasses.

We may note that there are three generally distinct temperature regimes in which different kinds of motion may be discussed, and each region is roughly determined by the thermal energy of the system. Motion at extremely low temperatures ($< 0.1 T_g$) is almost entirely localised and occurs between a pair of asymmetric, split-potential wells. Activation energies for such motion are low (≈ 0.1 eV) and motion manifests itself in a host of low-temperature anomalies. There is now a large and growing body of evidence to show that such split-potential wells (TLS) are a typical feature of the glassy state. In network glasses TLS may be visualised as involving motion in the network of bonds; in molecular or discrete ion glasses these may involve small changes in orientation of ions within their cages. Between 0.2 and $0.8 T_g$, both short range and long range motions begin to evolve within the glass. The strength of the absorption due to these motions is very low in lower temperature limits of this regime because of inherent broadening mechanisms. In this range of temperature activation barriers to motion range from 0.1 to 0.8 eV and the motion itself ranges from group motion to long range hopping. Dielectric and mechanical relaxations at higher temperatures in this range are complex, and many systems with diverse types of bonding appear to exhibit similar behaviour. Alkali ion motion in a variety of glasses also appears in this temperature range. Mixed ion effects, in particular, seem to display characteristic behaviour in dielectric and other studies. Beyond $0.8 T_g$, large scale particle motions begin to take place and separation of the various contributions is very difficult. Collective or cooperative movements that begin to appear in this region have still not been well understood even though Mossbauer experiments have provided significant information related to such motions.

Motion between $0.2 T_g$ and T_g strongly suggests the relevance of a cluster model as a basic ingredient of which is the existence of density fluctuations on a scale accessible to high resolution electron microscopy and small angle radiation or particle scattering. While experimental support for this model has been accumulating, modelling and analysis of particle motion remain to be carried out. It would be profitable to consider the presence of both density and composition fluctuations on a scale that does not lead to macroscopic phase separation. We have already pointed out that motion, particularly of ions involved in electrical conductivity, may be traced to motion either in the bulk region or on cluster surfaces.

from simulation studies on liquids that, unfortunately, do not tell much about behaviour in the glass. However, the importance of repulsive potentials on glass formation may be extended to discern patterns of particle motion. Such patterns may well be grouped on the basis of the softness of the repulsive potential and a study along these lines should be particularly useful in understanding particle motion in fast ion conducting glasses.

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Nitrogen NMR and molecular interactions

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1. Introduction

NMR is widely used as a means of obtaining information on molecular structure and the mechanisms of molecular reactions in given media. In order to provide unambiguous results of this kind it is necessary to have an understanding of the effects of the nuclear environment on the NMR spectrum of a particular molecule. Thus, medium effects are important in all NMR investigations as well as being of great interest in their own right.

Broadly speaking the term nuclear environment can encompass the influences of temperature, pressure and selectively chosen isotopes on the NMR parameters of a given nucleus in addition to that of the solvent and other solute molecules which may be present. In this paper we deal mainly with the effects of solute and solvent molecules on nitrogen NMR parameters which are obtained from an analysis of the positions and profiles of the signals appearing in an NMR spectrum.

The resonance positions and their relative intensities contain information relating to the shielding and spin-spin coupling interactions experienced by the nuclei. At the same time, relaxation contributes to the signal bandshapes and influences the evolution of resonance intensities under non-equilibrium conditions. All these NMR parameters are intimately related to the electronic environment of the nuclei concerned. Any subtle changes in environment are reflected in the appropriate NMR parameters which leads to the use of NMR as a probe of intermolecular forces and intramolecular force fields. Thus, in addition to structural and mechanistic detail, NMR may furnish fundamental information on the molecular environment extant at the time the spectrum is taken.

In recent years improvements in experimental techniques and instrumentation have led to large increases in the utilisation of both the ^{14}N and ^{15}N nuclei in NMR spectroscopy (Witanowski and Webb 1972, 1973; Witanowski *et al* 1977, 1981). Although the ^{14}N nucleus has by far the larger natural abundance it has an electric quadrupole moment while the less abundant ^{15}N nucleus does not. Thus, ^{14}N NMR studies are invoked when quadrupolar relaxation processes are to be investigated.

The larger magnetogyric ratio of the ^{15}N nucleus, together with its sharper NMR signals makes it more suitable for the determination of spin-spin interactions. In addition, the less efficient nuclear relaxation processes, such as those arising from magnetic dipole, spin-rotation, nuclear shielding anisotropy and scalar coupling interactions are usually studied by ^{15}N NMR.

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Nitrogen nuclear shieldings or chemical shifts, which are simply the differences in shielding between the nitrogen nuclei of interest and that of a given reference molecule such as nitromethane, are usually available from both ^{14}N and ^{15}N NMR spectra.

The complementarity of the NMR properties of ^{14}N and ^{15}N provides part of the basis for the use of nitrogen NMR in studies of molecular interactions. Other significant factors are the widespread importance of nitrogen in many areas of chemistry and the large variety of molecular environments in which nitrogen atoms may appear. This last factor is largely responsible for the fact that at about 900 ppm, the range of nitrogen chemical shifts in diamagnetic molecules is one of the largest found for nuclei of the first and second rows of the periodic table (Webb 1978).

The relationship between the various NMR parameters and molecular electronic structure has been adequately covered in recent reviews (Webb 1978; Ebraheem and Webb 1977; Kowalewski 1982) and is not repeated here. Some details of the measurement of media effects on nitrogen NMR parameters are provided in §2. We turn now to a consideration of some gas phase NMR phenomena.

1.1 Gas phase studies

It seems likely that the same mechanisms control intermolecular effects in the gaseous and liquid phases. Since advanced theoretical treatments of these effects deal more adequately with gases than with condensed phases, efforts have been made to study intermolecular effects by gas phase NMR. Small molecules are normally chosen for this work since anharmonic force fields are required as a test of the theoretical model chosen and these are usually only available for small molecules (Jameson 1981).

The nuclear shielding σ of an isolated molecule may be described for a dilute gas as a function of temperature T and density ρ by;

$$\sigma(T, \rho) = \sigma_0(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \dots \quad (1)$$

where the shielding parameter $\sigma_0(T)$, for a free molecule is a function of temperature due to averaging over various intramolecular motions and the terms containing ρ depict the intermolecular effects. The term $\sigma_1(T)$ is called the second virial coefficient of the nuclear shielding. For ^{15}N the range of values currently available, for σ_1 is from -0.0026 to -0.02 ppm/amagat where $1 \text{ amagat} = 2.687 \times 10^{19} \text{ molecules/cm}^3$ (Jameson 1981).

A ^{15}N NMR study of N_2O in the presence of CF_4 , SiF_4 and Xe has been reported from which it is observed that intermolecular interactions have a net deshielding effect on the nitrogen nuclei. The shielding change as a function of temperature and pressure is more marked for the terminal than for the central nitrogen nucleus in N_2O . This is consistent with the more exposed environment of the terminal nitrogen.

Some general conclusions are available from this and other studies on gaseous molecules. The value of σ_1 is always found to be negative such that a decrease in nuclear shielding is expected as the gas density increases. In general larger values of σ_1 tend to be more sensitive to temperature changes with the magnitude of σ_1 decreasing as the temperature increases. Nuclei with large chemical shift ranges tend to have larger σ_1 values, thus nitrogen nuclei are better placed than the more common NMR nuclei such as ^1H , ^{13}C , ^{19}F and ^{31}P . Finally, it is noted that more centrally located nuclei tend to have smaller values of σ_1 , N_2O provides a good example of this point.

As a consequence of these observations it follows that the temperature dependence of

increase in the nuclear shielding for a liquid sample at constant pressure is expected, whereas for the corresponding gas, measured at constant volume, the opposite is usually the case.

In order to obtain gas-to-liquid shielding changes the NMR sample should consist of a liquid in equilibrium with its vapour at a given temperature. Under these conditions the intramolecular terms, $\sigma_0(T)$ of equation (1), are removed and the difference between the gas and liquid NMR signals is due solely to intramolecular interactions. The signal from the liquid being deshielded with respect to that of the gas.

The ratio of the frequency difference between the two signals to the density difference between the gas and liquid phases provides an estimate of σ_1 if higher order terms in equation (1) are ignored.

The above comments apply to interactions between like molecules. For interactions between unlike molecules the shielding difference between the infinitely dilute solution, or pure liquid, and the zero pressure gas at the same temperature gives the total intermolecular contribution to the shieldings. For nuclei other than protons in non-polar media the range of gas-to-solution shifts can cover several ppm (Jameson 1981).

In general nuclei with large values of σ_1 tend to exhibit large solvent shifts in the condensed phase. Thus nitrogen NMR should be a very sensitive probe for condensed phase interactions.

1.2 Liquid state studies

In liquids, nitrogen nuclear shielding is perhaps the most sensitive of the NMR parameters to molecular interactions. However, changes in ^{14}N line widths due to such interactions can be appreciable and spin-spin coupling interactions may also be influenced.

In diamagnetic media non-specific solvent effects may produce significant nitrogen shielding changes as described in §3. These usually arise from interactions between the solute and solvent dipoles. Since most nitrogen containing molecules have fairly large dipole moments it follows that nitrogen NMR parameters are usually quite sensitive to non-specific solvent effects.

As well as contributing to the dipole moments of nitrogen containing molecules the lone pair electrons play a very important role in determining the magnitude of the paramagnetic component σ^p of the nitrogen shielding tensor.

As shown in equation (2) the total shielding σ depends upon both a paramagnetic term, σ^p and a diamagnetic term, σ^d where σ^d has a positive sign and σ^p a negative one

$$\sigma = \sigma^d + \sigma^p. \quad (2)$$

For molecules of a reasonable size, σ^d and σ^p are usually evaluated by semi-empirical molecular orbital techniques (Webb 1978). At this level of approximation σ^d is found to be roughly constant for nitrogen nuclei in a variety of environments (Jallali-Heravi *et al* 1979). Thus any change in σ arises from a variation in σ^p . Amongst other things σ^p depends rather critically on the reciprocal of certain electronic transition energies, such as $n \rightarrow \pi^*$. Consequently the presence or absence of the lone pair electrons, n , will significantly influence the nitrogen shielding.

An example of this effect is provided by the difference of 113 ppm between the nitrogen nuclear shielding of pyridine and the pyridinium ion. Protonation of the

nitrogen shielding of the pyrimidine ion is greater than that of pyrimidine. Other specific effects such as hydrogen bonding and self-association can have a similar effect on nitrogen shielding as discussed in §4.

Spin-spin couplings involving nitrogen nuclei are very dependent upon the orientation of the lone pair electrons and on whether they reside in *s* or *p* atomic orbitals (Tun Khin and Webb 1979). Similar arguments relate to the production of electric field gradients at a ^{14}N nucleus. Since the dominant quadrupolar relaxation process of ^{14}N depends upon the magnitude of such field gradients ^{14}N NMR signal widths can provide information on the position of lone pair electrons (Witanowski *et al* 1979). In principle, the lone pairs can make significant contributions to nitrogen shielding anisotropy (Jallali-Heravi and Webb 1978). However, this does not appear to be a very important ^{15}N relaxation process for most of the molecules studied to date.

Interactions involving lone pair electrons thus reveal themselves in changes in nitrogen nuclear shieldings, spin-spin couplings and in some relaxation processes. The lone pair can also play a critical role in interactions with paramagnetic centres as described in §5. Shift reagents are commonly used to simplify NMR spectra, such paramagnetic reagents can readily coordinate with nitrogen lone pair electrons.

In ^{15}N NMR studies relaxation reagents are often used to overcome problems associated with long dipolar relaxation times and NOE difficulties. Some of these reagents are quite specific for nitrogen (Levy *et al* 1978) and appear to interact with the lone pair electrons (Witanowski *et al* 1981).

1.3 Solid state studies

Traditionally solid state NMR has given rise to broad signals from which it has not often been possible to extract much chemically useful information. The most severe source of line broadening for solid samples is internuclear dipolar interactions. Overlapping resonances due to these interactions may be unravelled by means of two-dimensional NMR spectroscopy (Bodenhausen *et al* 1979). In the case of ^{14}N NMR signals, broadened due to proton-nitrogen dipolar coupling, the proton decoupled ^{14}N spectrum may be presented in one frequency domain while the second frequency domain consists of the dipolar splittings alone. Thus solid state dipolar interactions may be studied by this technique.

In recent years high resolution NMR spectra have become much more readily available from solid samples (Wasylishen and Fyfe 1982; Webb 1981). In such instances the dipolar interactions are removed by high power double resonance techniques. Additionally, magic angle sample spinning is employed to remove line broadening due to chemical shielding anisotropy relaxation which may be quite important for some nitrogen environments.

However, a residual solid state interaction between bonded nitrogen and carbon nuclei may appear as line broadening or splitting in the ^{13}C NMR spectrum (Groombridge *et al* 1980). This is not observed when ^{15}N replaces ^{14}N in the molecule of interest or in compounds having a small electric field gradient at the nitrogen site.

It seems likely that the interaction in question is due to opposing quantisation effects on the ^{14}N nucleus due to the internal electric field gradient on the one hand and the applied magnetic field on the other. Hence the interaction is expected to be reduced by

an increase in the nitrogen to carbon separation, an increase in the value of the applied field and/or a decrease in the nitrogen electric field gradient (Hexem *et al* 1981).

It may be concluded that the nitrogen lone pair electrons are important for this solid state interaction as they are for the various gaseous and liquid phase interactions mentioned previously.

2. Measurement of media effects by nitrogen NMR

2.1 Comparison of ^{14}N and ^{15}N techniques

Since the techniques of ^{14}N and ^{15}N NMR spectroscopy have already been considered in detail in a number of monographs and reviews (Randall 1973; Witanowski *et al* 1977; Levy and Lichter 1979; Martin *et al* 1981; Witanowski *et al* 1981), we intend to raise here only some points of relevance to investigations of molecular interactions.

As far as nitrogen shieldings are concerned, those obtained from ^{14}N and ^{15}N measurements are essentially interchangeable (Witanowski *et al* 1977, 1981). From the experimental data (Schultheiss and Fluck 1977) one can estimate indirectly that differences between ^{14}N and ^{15}N shieldings for the corresponding isotopomers should not exceed 0.2–0.3 ppm. One should note that in a recent monograph (Martin *et al* 1981) such isotope effects are erroneously reported as larger by an order of magnitude (*i.e.* up to 2–3 ppm) due to a mistake in the recalculation of the original data.

Effects of molecular interactions on nitrogen shieldings can be quite large, but there are several sources of experimental error which can either obscure or adversely affect their appearance in the spectra. Since the ^{15}N nucleus (natural abundance 0.36%) has a spin of 1/2 and no quadrupole moment, the corresponding resonances are rather sharp, and the precision of estimating differences between their positions in the *same* spectrum can reach 0.1 ppm or better, provided that the signal-to-noise ratio is better than 10. Otherwise, the position of the peak of the signal can be affected to the extent of approximately one half-height width of the signal concerned, and this can amount to errors of 0.5–1 ppm. The ^{14}N nucleus (99.64% natural abundance) has a spin of 1 and a non-zero electric quadrupole moment, the corresponding resonance signals have half-height widths ranging from a few Hz to several kHz. Their widths can severely hamper the resolution and the precision of estimating the positions of the signals. Therefore, any precise measurement of nitrogen shieldings by ^{14}N NMR must involve signal lineshape fitting. Such methods, particularly when coupled with the differential saturation technique (Witanowski *et al* 1981, and references therein), can afford a precision of 0.1 ppm or better in ^{14}N NMR measurements, even for overlapping broad signals.

It is not sufficient, however, to rely on the precision of relative positions of nitrogen resonance signals from the point of view of effects of molecular interactions, particularly when different spectra are compared. There are other sources of error which can be of the same order of magnitude as the molecular interaction effects on nitrogen shielding in the molecules considered. These come mainly from bulk magnetic susceptibility effects, the use of unreliable standards for calibration of the spectra, and from using certain additives, such as relaxation reagents which are frequently employed in ^{15}N NMR spectroscopy.

One of the most severe problems is that of referencing nitrogen shieldings

No internal reference substance (one dissolved in the sample) is immune to intermolecular effects on its nitrogen shielding (Witanowski *et al* 1977). This excludes internal referencing from use in investigations of molecular interactions by nitrogen shieldings. Some exceptions are possible in measurements for paramagnetic systems when the disturbances in the shielding of an internal reference by intermolecular effects are smaller than the bulk susceptibility effects involved in the use of external standards. Thus, the most reasonable method is to employ an external reference in a system of separate containers for the sample and the standard, respectively. The recommended external reference for both ^{14}N and ^{15}N measurements is neat liquid nitromethane, CH_3NO_2 (Witanowski *et al* 1977, 1981; Levy and Lichter 1979; Martin *et al* 1981), but it is not reasonable to recalculate data referred directly to nitromethane as external standard to another reference system, based for example on neat NH_3 (Levy and Lichter 1979). The latter procedure, if used indiscriminately, can lead to serious errors resulting from bulk susceptibility effects, as indicated in a recent monograph on nitrogen NMR (Witanowski *et al* 1981). The use of an external standard for the calibration of nitrogen shieldings results in the appearance of effects due to differences in volume magnetic susceptibilities between sample and standard. The problem (considered in §2.2) can hardly be evaded in ^{15}N NMR, since obtaining high-resolution spectra of ^{15}N nuclei requires sample spinning, and the only practical arrangement in this case is that of coaxial tubes, with the reference usually placed in the inner tube. The use of concentric spherical containers, which eliminate the susceptibility effects is practical only in ^{14}N NMR, where the relatively large signal widths make sample spinning useless from the point of view of signal improvement. The problem of bulk susceptibility effects on apparent nitrogen shieldings is even more acute in ^{15}N spectroscopy when paramagnetic relaxation reagents are employed to shorten the long relaxation times of ^{15}N in nitrogen atoms which are not bound directly to hydrogen atoms (see §§2.2 and 2.3).

It seems that ^{14}N NMR can be profitably exploited to examine intermolecular effects for small to medium-sized molecules, since the application of the lineshape fitting method, the differential saturation technique and concentric spherical sample containers should yield high-precision data on changes in nitrogen shielding in various media. In contrast to this, ^{15}N NMR offers high-resolution spectra which are particularly suitable for the estimation of nitrogen shielding in the cases of large molecules, large numbers of non-equivalent nitrogen atoms, and viscous media, at the cost of the problem of precise calibration of the shieldings on any scale based on a common reference. Some examples should clarify the points raised here. It would be difficult, if not impossible, at least at magnetic fields currently available, to precisely follow changes in the nitrogen shielding of individual nitrogen atoms upon changing the acidity of the aqueous medium in a complicated molecule such as that given in table 14 from its ^{14}N NMR spectra, because of relatively small differences in the shielding between the nitrogen atoms when compared with the ^{14}N signal widths which are typical for hydrogen-bonded NH and NH_2 groups in large molecules (they can be of the order of kHz). The problem is easily solved in the high-resolution ^{15}N spectra (table 14) and the question of bulk susceptibility effects, reference substances, and paramagnetic additives is not important from the point of view of *differences* in the shielding between the spectra, since only aqueous media are involved, and the ^{15}N nuclei in NH and NH_2 groups usually relax sufficiently rapidly so as not to require the use of relaxation reagents. On the other hand, the high-precision data from ^{14}N nuclei

on the effects of paramagnetic relaxation reagents on nitrogen shieldings (table 2) or those on medium effects on nitroalkanes (table 4) could not be reproduced simply and reliably by ^{15}N methods.

Spin-spin couplings with nitrogen nuclei can also be employed for the investigation of molecular interactions, but since ^{14}N nuclei usually relax very rapidly due to the quadrupole relaxation mechanism, only a small number of results are available on ^{14}N couplings, and the vast majority of measurements in this field come from ^{15}N NMR spectra or those of nuclei coupled to ^{15}N (Witanowski *et al* 1977, 1981). Recently, methods based on spin polarization transfer to ^{15}N from stronger magnetic dipoles (*e.g.* protons) greatly facilitate obtaining spin-spin coupling constants of ^{15}N either directly from ^{15}N spectra or from ^{15}N satellites in the spectra of other nuclei (Martin *et al* 1981, and references therein). If necessary, one can recalculate ^{14}N coupling constants to the corresponding ^{15}N coupling constants, or *vice versa*, using the relation

$$J(^{14}\text{N-X}) = -0.7129 J(^{15}\text{N-X}). \quad (3)$$

The relaxation of nitrogen nuclei can also be used for the investigation of molecular interactions, mostly those which affect molecular rotations and those involving paramagnetic centres. There are a number of routine methods of measuring ^{15}N relaxation times (Levy and Lichter 1979, and references therein), and high-resolution spectra of ^{15}N offer the possibility of simultaneous observations of ^{15}N relaxation rates for different nitrogen atoms within a molecule. The weakness of the method of following molecular interactions by means of ^{15}N relaxation measurements lies in the fact that ^{15}N relaxation times are usually quite long (up to 100 sec) and as such can be grossly affected by a variety of factors, including the presence of paramagnetic impurities in trace amounts. The fast relaxation rates of ^{14}N , where the quadrupolar relaxation is dominant, are much less affected by spurious effects, and can be measured by routine techniques (Lehn and Kintzinger 1973). There is, however, a problem with resolving the rates for non-equivalent nitrogen atoms where such are present in the sample examined. The differential saturation technique combined with lineshape fitting (Witanowski *et al* 1981, and references therein), used for obtaining precise data on ^{14}N shieldings, can be routinely exploited for the measurement of ^{14}N relaxation times in systems of non-equivalent nitrogen atoms.

2.2 Bulk susceptibilities

If the method of external referencing is used for the calibration of nitrogen shieldings one has to consider the effect of experiencing different magnetic fields, on the nuclei in the sample and the standard employed, which results from the corresponding differences in volume magnetic susceptibilities. Problems concerned with such effects have been considered generally (for example, Rummens 1975), but we shall limit ourselves to those for concentric sample containers with the standard in the inner container. The general equation for the true difference between the screening constants, σ , of the sample and the reference is as follows

$$(\sigma_{\text{sample}} - \sigma_{\text{ref.}})_{\text{true}} = (\sigma_{\text{sample}} - \sigma_{\text{ref.}})_{\text{observed}} - \left(\frac{4}{3}\pi - \alpha\right)(\chi_{\text{ref.}} - \chi_{\text{sample}}), \quad (4)$$

where χ is the corresponding magnetic volume susceptibility, and α is a factor

- $\alpha = 0$ for concentric cylinders and magnetic field parallel to their common axis, cylinders spinning around this axis;
- $\alpha = 2\pi$ for concentric cylinders and magnetic field perpendicular to their common axis, cylinders spinning around this axis;
- $\alpha = 4\pi/3$ for spherical containers, no effects due to spinning.

Thus, the correction to the apparent shielding difference vanishes for spherical containers, but for concentric cylindrical tubes it depends not only on the susceptibility difference involved, but also on the direction of the magnetic field (the arrangement is typical of superconducting magnets, and the perpendicular orientation between the field and the axis of the cylinders is typical of electromagnet systems). Corrections which should be added algebraically to apparent shieldings in NMR solutions in a variety of solvents, when neat nitromethane is employed as an external standard, are given in table 1. Corrections for other standards, provided their susceptibilities are known, can be obtained from those in table 1 by simple algebraic subtraction of the correction for the standard employed, with respect to nitromethane, from the values given in the table. One should note that corrections for the parallel arrangement of the field and the cylinder axis are twice as large in magnitude as those for the perpendicular arrangement, and are opposite in sign. The diamagnetic effects of diamagnetic (*i.e.* negative) volume susceptibilities can be large enough to seriously disturb observations of intermolecular effects on nitrogen shielding when the effects are of the order of a few ppm. This is particularly true for superconducting magnet systems. Introducing corrections for such effects is not always straightforward, since the susceptibility of the sample examined is frequently not known, and the geometry involved pertains to infinitely long cylinders, while the large-bore samples commonly employed in ^{15}N spectroscopy, in order to increase sensitivity, significantly from the ideal geometry assumed. The situation becomes even more critical when paramagnetic systems are examined or when paramagnetic impurities or additives are present in samples. Such substances can add quite large paramagnetic (positive) components to volume magnetic susceptibilities, and their effects can be much greater than those given in table 1. It is therefore mandatory in any investigation of molecular interactions to try to eliminate bulk susceptibility effects either by calculated corrections or by the use of spherical samples. In any case it is important to specify exactly the experimental conditions, standards, compositions, and methods of correction employed.

2.3 Relaxation reagents

Since the relaxation times of ^{15}N nuclei are often quite long, and can be prohibitively long spectrum accumulation times, in order to obtain any reasonable signal-to-noise ratio in ^{15}N spectra it has become a common practice in NMR spectroscopy to reduce ^{15}N relaxation times by molecular interactions of the complexation type between the nitrogen atoms concerned and chelated cations such as Cr(III) or Gd(III) . The most popular paramagnetic additive (relaxation reagent)

Table 1. Corrections for volume bulk magnetic susceptibilities for diamagnetic dilute solutions^a.

Solvent	Its volume susceptibility (at 30°C) $\times 10^6$	Correction to observed nitrogen shielding (in ppm) referred to neat nitromethane in coaxial cylinders with nitromethane in inner cylinder	
		Perpendicular to magnetic field	Parallel to magnetic field
MeNO ₂	-0.387	0	0
Acetone	-0.456	+0.14	-0.28
MeCN	-0.518	+0.27	-0.54
MeOH	-0.523	+0.28	-0.56
Et ₂ O	-0.522	+0.28	-0.56
MeCOOH	-0.549	+0.34	-0.68
n-hexane	-0.558	+0.36	-0.72
MeNH ₂	-0.564	+0.37	-0.74
EtOH	-0.569	+0.38	-0.76
n-BuNH ₂	-0.591	+0.43	-0.86
Dioxan	-0.591	+0.43	-0.86
Pyridine	-0.597	+0.44	-0.88
Benzene	-0.609	+0.46	-0.92
HNO ₃ 70 %	-0.618	+0.49	-0.98
Cyclohexane	-0.623	+0.49	-0.98
DMSO	-0.618	+0.49	-0.98
CCl ₄	-0.684	+0.62	-1.24
CS ₂	-0.693	+0.64	-1.28
H ₂ O	-0.716	+0.69	-1.38
CH ₂ Cl ₂	-0.717	+0.69	-1.44
H ₂ SO ₄ 100 %	-0.723	+0.70	-1.40
CHCl ₃	-0.730	+0.72	-1.44
CH ₂ Br ₂	-0.932	+1.14	-2.28

^a see Witanowski *et al* 1977; also Witanowski *et al* 1981, and references therein.

shown in the preceding section. Large artifacts in the observed shieldings for ¹⁵N in nitroaromatic compounds, upon addition of Cr(acac)₃, have been found to originate from such effects (Schuster and Roberts 1980). Bulk susceptibility effects of this kind can be eliminated, at least in principle, by measuring the susceptibilities (*e.g.* from the corresponding proton spectra in non-spinning coaxial tubes) and introducing due corrections (see the preceding section). However, there is always the question of intrinsic shifts in nitrogen shieldings induced by the presence of relaxation reagents. Recent high-precision ¹⁴N data (Witanowski *et al* 1981) on shifts induced by some relaxation reagents (table 2) show that Cr(acac)₃ does not introduce significant changes in nitrogen shieldings, with the exception of basic sites such as pyridine-type nitrogen atoms, at concentrations which are effective from the point of view of reducing the relaxation times. However, reagents of the spin-label type (those acting preferentially

Table 2. Nitrogen shielding changes induced by some relaxation reagents^a.

Compound (neat liquid)	Change in nitrogen shielding (in ppm, referred to that in neat liquid) upon addition of the reagent specified	
	Cr(acac) ₃ 1:100 molar ratio	Gd(dpm) ₃ 1:1000 molar ratio
MeNO ₂	-0.07 ± 0.06	Reagent insoluble
Me-N=C=O	-0.12 ± 0.10	-0.18 ± 0.12
HCONMe ₂	+0.12 ± 0.11	+1.06 ± 0.12
Me-CN	-0.02 ± 0.11	-0.04 ± 0.11
Pyridine	+0.41 ± 0.12	+6.61 ± 0.16
NEt ₃	reagent insoluble	+0.99 ± 0.18
Me-N=C=S	+0.21 ± 0.10	+0.28 ± 0.07

^a ¹⁴N data from Witanowski *et al* 1981, concentric spherical sample/standard containers in order to eliminate bulk susceptibility effects; acac = (MeCOCHCOMe)⁻, dpm = (Me₃CCOCHCOMe₃)⁻.

shieldings, and one should be wary of the sources of possible errors in the interpretation of nitrogen shielding changes measured in the presence of relaxation reagents.

2.4 General survey of media effects on nitrogen shieldings and spin-spin couplings

Among the parameters available from the measurement of nitrogen NMR spectra, nitrogen shieldings are probably most useful as far as investigations of molecular interactions are concerned, since they reveal strong responses to various types of interactions. Since there are various conventions concerning signs and references for the so-called chemical shifts in NMR, and particularly in nitrogen NMR (Witanowski *et al* 1981; Martin *et al* 1981; Levy and Lichter 1979), we adopt a system of expressing nitrogen chemical shifts in terms of differences in the magnetic shielding between the nucleus examined and the reference used, so that a positive value denotes an increase in shielding. As a general-purpose reference we use the nitrogen shielding of neat liquid nitromethane. We do not use the term 'chemical shift' in order to avoid confusion concerning the sign of its value. The sensitivity of nitrogen shielding to molecular structure is reflected in the response of the shielding to molecular interactions in liquid media, as shown in table 3. There seems to be a considerable influence on the shielding of some bulk properties of the media involved, particularly the dielectric constant (§3). Such effects seem to emerge from changes in electron charge distribution in a solute due to interactions with charges induced by the solute in the surrounding medium (§3.2). It is important to note that relative effects of this kind on nitrogen shielding are most pronounced for low values of the dielectric constant, and they are considerably quenched for values in excess of about 10. If one wants to investigate specific molecular interactions by means of nitrogen shieldings, one should be wary of the possible non-specific interaction effects which appear when media with low and high dielectric constants are compared. The safest way is to compare media with high dielectric constants when specific interactions are examined, if there are no reliable estimates of the bulk polarity effects of the medium on the nitrogen shieldings in the molecules

Table 3. Major effects on nitrogen shielding due to molecular interactions in liquids

Type of interaction	Maximum observed range of effects on nitrogen shielding (ppm)	Comments
Bulk dielectric constant of medium—solute	10	Largest effects within low values of the constant (up to <i>ca</i> 10)
Hydrogen bonding	35	Largest effects for multiply-bonded nitrogen atoms with lone electron pairs which do not participate in conjugated π -electron systems
Association and complexation with diamagnetic molecules and ions	40	
Interactions with paramagnetic centres	Several thousand	Largest effects are due to unpaired spin delocalization over nitrogen atoms
Protonation-deprotonation equilibria	150	Largest changes upon protonation of multiply-bonded nitrogen atoms with lone electron pairs.

The bulk polarity effects of various media on nitrogen shielding are interesting, such, since they reflect structural changes in the solute molecules induced by interaction with the solvent molecules.

As far as specific interactions are concerned, nitrogen shielding provides a sensitive probe to protonation-deprotonation equilibria (table 3 and §4.2), since the range of effects extends beyond 100 ppm. For nitrogenous compounds, nitrogen shieldings and couplings provide the most effective tool among NMR methods for tracing interactions with proton-donating and proton-accepting media.

Hydrogen-bonding effects on nitrogen shieldings are also appreciable (table 3, §4.1), and can be employed profitably for the examination of interactions of this nature. However, one should be wary of the fact that very often the direction of hydrogen-bonding effects on nitrogen shielding is parallel to those due to protonation, and the bulk polarity effects of media can compete with hydrogen-bonding in the overall pattern of changes in nitrogen shieldings. Theoretical explanations of the magnitude and direction of hydrogen bonding effects in some typical situations have recently become available for nitrogen shieldings (§4.1, tables 7 and 9).

Other specific interactions in diamagnetic systems can also produce significant effects on nitrogen shielding (§4.3), but their nature, in most cases, has not been explained in terms of any rigorous theory. Nevertheless, such changes in nitrogen shielding have practical applications in detecting the participation of nitrogen atoms in specific interactions.

Specific interactions with paramagnetic molecules and ions can lead to very large changes in nitrogen shielding, particularly when nitrogen atoms bearing lone electron pairs are involved directly in complexation with a paramagnetic centre, as shown in table 3 and §5. Thus, even if the mole fractions of interacting nitrogen atoms are small, there are usually significant changes in nitrogen shielding when averaged over all interacting and non-interacting nuclei.

Spin-spin couplings between nitrogen and other nuclei can also reveal the effects of

absolute values of one bond ^{15}N - ^1H couplings. The presence or absence of easily distinguishable multiplet patterns resulting from the coupling, or dynamic changes in such multiplets, provide precise information about proton exchange processes in liquid media. They also afford a simple method for distinguishing between intra- and inter-molecular proton exchange. There are quite significant effects, due to the protonation of molecules in proton-donating media, on the values of ^{15}N couplings whose appearance in the ^{15}N spectra is not affected by the rate of proton exchange processes.

3. Non-specific solvent effects

The modern techniques in use in nitrogen NMR have given rise to the production of accurate data on fairly dilute solutions, and thus to an appreciation of the importance of solvent effects on nitrogen NMR parameters. The range of solvent effects on nitrogen shielding can be comparable to that of substituent effects or those due to other structural modifications of the molecule (Witanowski *et al* 1981). Consequently solvent effects have to be taken account of in studies which aim at relating nitrogen NMR parameters to molecular structure.

Intermolecular solute-solvent interactions can be considered to be of either the non-bonded or the bonded type. The former of these is dealt with in this section while §4 covers bonded interactions such as protonation, hydrogen bonding, molecular association, ionic interactions, aromatic solvent induced shifts, intramolecular charge and magnetic equivalence effects (Homer 1978).

The non-bonded interactions thought to be most likely to influence NMR parameters are bulk susceptibility effects, Van der Waals effects neighbour susceptibility anisotropies and electric field influences. It is generally considered that these operate by means of an electrostatic interaction between the solute and solvent molecules (Buckingham 1960). Consequently, they are often referred to as non-specific interactions and may reasonably be described by a model containing an account of the charge distribution in the interacting molecules.

Non-specific solute-solvent interactions are frequently discussed in relation to two types of model. In one type the interaction is described by a pair of molecules, in the other type the solvent is considered as a continuum and its bulk properties such as dielectric constant and refractive index are correlated with the observed change in NMR parameters. Since it is experimentally rather difficult to estimate the relative importance of the various non-specific interactions (Homer 1975) it seems inherently reasonable to adopt a continuum model for the interpretation of non-specific solvent effects on NMR parameters.

3.1 Some models for non-specific solvent effects

Before turning to the continuum models we deal briefly with the pair interaction model of non-specific solvent effects.

Although it has been applied to nuclear shielding changes in condensed phases the pair interaction model strictly applies only to the dilute gas phase. It has been moderately successful in dealing with some ^1H and ^{19}F data but, so far has not been applied to nitrogen NMR results (Jarnsen 1981). The omission of a method for

solution nuclear shielding changes (Jameson 1981). A particular advantage of models of this kind is that they employ parameters characteristic of bulk samples, which are usually well known.

Most continuum models of interest from the NMR point of view are based upon Onsager's reaction field model (Onsager 1936), which has been very successful in the development of the theory of dielectrics. In Onsager's model a solute molecule is considered to be surrounded by a uniform dielectric medium arising from the solvent molecules. The spontaneous oscillating dipole moment of the non-polar solute molecule is predicted to polarise the continuum which in turn creates a reaction field at the site of the solute. Equilibrium is then reached between the oscillating moment and the reaction field from which the dispersion energy and mean square field may be estimated.

A polar solute molecule is represented by a point dipole at the centre of a spherical solvent cavity. In this case the solvent is described by a continuum of static dielectric constant.

Several continuum models have been based on that of Onsager and applied to solvent effects on NMR parameters. Comprehensive reviews and analyses of these models are available (Homer 1975; Rummens 1975).

Typically the reaction field R is given by

$$R = \frac{2\mu(\epsilon - 1)(n^2 - 1)}{3\alpha(2\epsilon + n^2)}, \quad (6)$$

where n is the refractive index of the solute, α is its polarisability, μ refers to the solute point dipole and ϵ is the dielectric constant of the solvent. The resulting induced change in the nuclear shielding, $\Delta\sigma$, is given by

$$\Delta\sigma \propto \frac{(\epsilon - 1)}{2\epsilon + n^2}.$$

Equation (6) and others similar to it, provides an opportunity for systematically classifying solvent effects on chemical shifts. Some success has been obtained with solution chemical shift and spin-coupling data by this approach. However, it appears that continuum models are not of general applicability to the interpretation of gas-liquid or gas-to-infinitely dilute solution studies (Jameson 1981). For a unified interpretation of solvent effects it seems likely that details of the structures of liquid mixtures will need to be incorporated into the theory (Barfield and Johnston 1979).

Until such a comprehensive theory becomes available for molecules of chemical interest other approaches are worthy of consideration. One such procedure, which incorporates semi-empirical molecular orbital calculations, employs the Solvaton model (Ando and Webb 1981). Since this has been successfully applied to nitrogen nuclear shielding and spin-spin couplings it is discussed here in some detail.

3.2 Solvaton model and some of its applications

The Solvaton model represents the oriented solvent distribution around each atom of the solute molecule. At infinite dilution of the solute it is assumed that a number of charges (Solvatons) are induced in the solvent. Further it is necessary to consider the solute molecule as a Solvaton whose charge is equal to the sum of the charges of the

magnitude, but opposite in sign, to that of the atom with which it is associated there are no interactions between Solvatons and that the strength of the mol Solvaton interaction depends upon the polarity of the solvent as expressed dielectric constant. From these considerations it is clear that the Solvaton provides an application of the reaction field model to NMR parameters. Further ev for this point of view is available from the fact that the nuclear shielding chang depend upon the dielectric constant in the manner

$$\Delta\sigma \propto \frac{\epsilon - 1}{2\epsilon}$$

within the Solvaton model, which is analogous to equation (6).

In discussing NMR parameters the Solvaton model has been used in conjunction various semi-empirical molecular orbital schemes (Ando and Webb 1981). For ni nuclear shielding it seems that sum-over-states (sos) perturbation calculation incorporating INDO/S parameters are the most reliable to date.

The results of a study on nitromethane, ammonia, pyridine, methylcy methylisocyanide and nitrate ion show that changes in nitrogen nuclear shieldin nitrogen charge density, as a function of ϵ , are not necessarily parallel (Ando *et al*). This is attributed to the fact that the nuclear shielding changes are control variations in the paramagnetic component which is not normally expected to d linearly on charge density differences (Ebraheem and Webb 1977).

In some cases, nitromethane and methyl cyanide, the nitrogen screening is pre to decrease as ϵ increases, whereas the opposite is true for the other species consi. The available experimental data support these predicted trends and lend credence Solvaton model when used in conjunction with INDO/S parametrised sos calculati nuclear shielding.

In the case of pyridine the experimental results reveal that both non-specific hydrogen bonding effects influence the nitrogen shielding (Kolling 1979). interpretation is supported by the INDO/S parametrised Solvaton model calcula.

Similar calculations of the nitrogen shielding as a function of ϵ have been repor a number of nitroalkanes (Witanowski *et al* 1981). In all cases the shielding is pre to decrease as ϵ increases which is in line with the experimental data as shown in t. The experimental results are of a high precision on account of the data proc techniques used (Witanowski *et al* 1981). In addition they were obtained by the concentric spherical sample and reference containers which remove bulk suscep effects from the observed shielding changes. It is noteworthy that the choice of so used is such as to minimise specific solute-solvent interactions. Thus the presented in table 1 yield shielding variations due to influences inherent to the re field description and provide a good test of the Solvaton model.

Comparison of the results of the calculations with the observed shielding cl shows that in all cases considered there is very good agreement both on the direc the change, a shielding decrease as ϵ increases, and on the magnitude of the cl observed in various solvents.

As a result of this study it is apparent that in the solvents chosen the ni shielding changes of the nitroalkanes are due to non-specific solute-solvent intera which result in electronic redistributions in the molecules concerned. It follow since the dielectric constants of the neat nitroalkanes considered differ consid

Table 4. Comparison of calculated and observed solvent effects on the nitrogen shielding of some nitro-alkanes.

Compound	Solvent (0.3 M solutions)	Dielectric ϵ , at 30°C	^{14}N shielding (ppm)	
			Observed with re- spect to neat CH_3NO_2	Calculated
CH_3NO_2	DMSO	45.8	-2.01 ± 0.12	-0.6
	DMF	37.5	-0.69 ± 0.13	-0.5
	None	35.9	0.0000	-0.4
	CH_3CN	36.6	0.20 ± 0.13	-0.4
	Acetone	20.4	0.77 ± 0.10	0.0
	CH_2Cl_2	9.5	3.21 ± 0.12	1.3
	CH_2Br_2	6.78	3.41 ± 0.12	2.3
	CHCl_3	5.07	3.79 ± 0.13	4.3
	Diethyl ether	4.79	3.91 ± 0.13	4.8
	CCl_4	2.71	7.10 ± 0.11	8.8
$\text{CH}_3\text{CH}_2\text{NO}_2$	DMSO	45.8	-11.37 ± 0.16	-10.6
	None	28.1	-10.25 ± 0.10	-10.4
	Acetone	20.4	-9.37 ± 0.11	-10.2
	CCl_4	2.71	-4.09 ± 0.12	-4.4
$\text{CH}_3(\text{CH}_2)_2\text{NO}_2$	DMSO	45.8	-10.09 ± 0.21	-9.8
	None	23.2	-7.73 ± 0.10	-9.3
	Acetone	20.4	-8.31 ± 0.14	-9.2
	CCl_4	2.71	-3.77 ± 0.16	-1.5
$(\text{CH}_3)_2\text{CHNO}_2$	None	25.5	-19.45 ± 0.10	-19.3
	Acetone	20.4	-19.40 ± 0.15	-19.2
	CCl_4	2.71	-14.73 ± 0.14	-15.1
	DMSO	45.8	-28.20 ± 0.17	-27.9
$(\text{CH}_3)_3\text{CNO}_2$	Acetone	20.4	-25.95 ± 0.11	-27.4
	None		-25.51 ± 0.11	
	CCl_4	2.71	-21.57 ± 0.12	-21.4

measurements made on dilute solutions in the same solvent, rather than on neat liquid samples.

Due to its successful prediction of the nitrogen shielding changes found in the nitroalkanes, further applications of the Solvaton model for non-specific interaction effects on nitrogen NMR parameters are to be expected. For example the effects of solvents on the nitrogen chemical shifts of α amino acids appear to operate through a variety of mechanisms, some involving the carboxylate group others the ammonium group (Kricheldorf 1979). It should be possible to unravel these various contributions by means of the Solvaton model. Similarly, the various contributions to the solvent dependence of 1J (N-C) for acetamide (Kricheldorf 1980) may be better understood as a result of involving the solvaton model.

Observed nuclear spin-spin couplings, J_{obs} , are usually considered to consist of three possible contributions as indicated by equation (8)

$$J_{\text{obs}} = J_c + J_o + J_D, \quad (8)$$

where J_c , J_o and J_D refer to contact, orbital and dipolar interactions respectively (Webb 1978).

At the present initial level of molecular orbital calculations the contact term is the

between pairs of either nuclei or three of the terms presented in equation (8) may contribute and in principle, all may be solvent dependent (Ando and Webb 1981).

Table 5 shows the results of some sos perturbation calculations of $^1J(\text{N-C})$ as a function of ϵ obtained from the Solvaton model incorporating INDO parameters (Shargi and Webb 1981). For acetamide $^1J(\text{N-C})$ is predicted to be negative in sign and dominated by the contact term. In addition the magnitude of $^1J(\text{N-C})$ decreases by about 0.2 Hz as ϵ increases in value from unity, corresponding to the isolated acetamide molecule, to 40.

Similar comments apply to the other $^1J(\text{N-C})$ data presented in table 2. It is not surprising that $^1J(\text{N-C})$ is dominated by the contact contribution for most of the cases considered (Tun Khin and Webb 1977). However, it is interesting to note that the Solvaton model predicts that some values of $^1J(\text{N-C})$ will increase while others will decrease by a similar amount as ϵ varies. A particular case in point is the pair of $^1J(\text{N-C})$ results for $(\text{CH}_3)_2\text{NCHO}$. Clearly, non-specific solvent effects have to be taken into account in the interpretation of these spin-spin coupling data. The predicted increasingly negative value of $^1J(\text{N-C})$ for formamide as ϵ increases, is in agreement with the available experimental data (Hinton *et al* 1973).

For pyridine the change in $^1J(\text{N-C})$ is larger, the magnitude decreases by about 0.5 Hz as ϵ ranges from unity to 40, mainly due to a variation in the dominating orbital contribution and the contact term. This more pronounced $^1J(\text{N-C})$ variation reflects the importance of the nitrogen lone pair electrons in spin-spin couplings and in solvation interactions.

As befits a charged species, $^1J(\text{N-C})$ for the pyridinium ion changes in magnitude by 5.5 Hz over the dielectric constant range considered in table 5. This indicates a strong interaction between the ion and polar media.

The values of $^1J(\text{N}\equiv\text{C})$ for the cyanide and isocyanide examples given in table 5 have significant contributions from the dipolar interaction as observed previously (Tun Khin and Webb 1978). The variation of $^1J(\text{N}\equiv\text{C})$ by about 1 Hz over the range of ϵ considered, for the cyanide and isocyanide is largely due to a variation in the contact term. This again implies an interaction with the solvent involving the nitrogen lone pair electrons since these may make a significant contribution to the contact term. Whereas the orbital and dipolar interactions are controlled, at the semi-empirical level, by the distribution of p electrons.

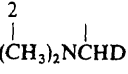
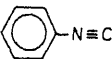
From these results it seems likely that spin-spin couplings involving nitrogen nuclei will be dependent on non-specific solvent effects. Particularly in the case of charged species and in those instances where the nitrogen lone pair electrons are readily available for interaction with the surrounding medium.

4. Specific medium effects in diamagnetic systems

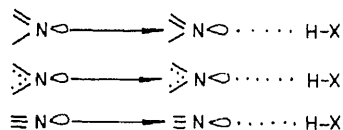
4.1 Hydrogen bonding

Hydrogen bonding effects on nitrogen shielding are often appreciable (tables 3 and 6), but their magnitudes and signs depend critically on the nitrogenous structures involved. However, the detection of such effects can be significantly disturbed by the medium polarity effects described in §3, particularly when one compares media with low dielectric constants (*e.g.* hydrocarbon solvents) and hydrogen-bonding solvents which are usually characterized by high dielectric constants. Therefore, the data in

Table 5. Some calculated solvent effects on the various contributions to one-bond nitrogen-carbon couplings, in Hz.

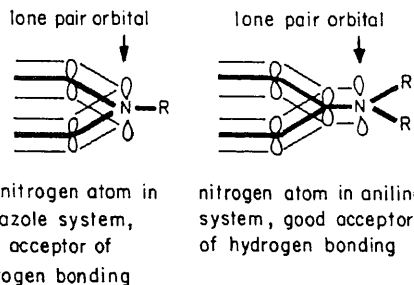
Compound	Coupling	Coupling contributions	Dielectric constant ϵ				
			1	4	8	20	40
<chem>CH3CONH2</chem>	$^1J(\text{N-C})$	J_C	-8.748	-8.619	-8.597	-8.584	-8.579
		J_O	-1.478	1.528	1.538	1.543	1.545
		J_D	0.035	0.022	0.019	0.018	0.018
		J_{total}	-7.235	-7.069	-7.040	-7.023	-7.016
<chem>NH2CHO</chem>	$^1J(\text{N-C})$	J_C	-12.533	-12.412	-12.395	-12.381	-12.378
		J_O	1.688	1.748	1.756	1.767	1.769
		J_D	0.052	0.032	0.028	0.026	0.025
		J_{total}	-10.793	-10.632	-10.611	-10.588	-10.484
<chem>CH3NH2</chem>	$^1J(\text{N-C})$	J_C	-10.618	-10.500	-10.478	-10.464	-10.455
		J_O	0.611	0.613	0.613	0.613	0.613
		J_D	-0.238	-0.238	-0.238	-0.238	-0.238
		J_{total}	-10.245	-10.129	-10.105	-10.091	-10.082
<chem>(NH2)2CO</chem>	$^1J(\text{N-C})$	J_C	-16.810	-17.000	-17.038	-17.056	-17.062
		J_O	1.312	1.347	1.354	1.358	1.359
		J_D	0.006	-0.005	-0.007	-0.008	-0.008
		J_{total}	-15.492	-15.658	-15.691	-15.706	-15.711
	$^1J(\text{N-C})$	J_C	-13.788	-13.870	-13.885	-13.894	-13.896
		J_O	1.521	1.554	1.561	1.565	1.566
		J_D	-0.012	-0.017	-0.018	-0.018	-0.019
		J_{total}	-12.279	-12.343	-12.342	-12.347	-12.349
	$^1J(\text{N-C})$	J_C	-4.309	-4.192	-4.171	-4.159	-4.155
		J_O	0.457	0.458	0.458	0.458	0.458
		J_D	-0.202	-0.202	-0.203	-0.203	-0.203
		J_{total}	-4.054	-3.936	-3.916	-3.904	-3.900
	$^1J(\text{N-C})$	J_C	0.986	0.619	0.551	0.509	0.495
		J_O	3.051	3.032	3.029	3.027	3.026
		J_D	-0.138	-0.136	-0.136	-0.136	-0.136
		J_{total}	3.899	3.515	3.444	3.400	3.385
	$^1J(\text{N-C})$	J_C	-10.802	-7.765	-7.765	-6.693	-6.553
		J_O	2.265	2.472	2.509	2.533	2.541
		J_D	0.108	-0.133	-0.126	-0.128	-0.128
		J_{total}	-8.479	-5.416	-4.723	-4.288	-4.140
<chem>CH3C#N</chem>	$^1J(\text{N}\equiv\text{C})$	J_C	3.596	2.848	2.716	2.636	2.608
		J_O	-3.997	-3.787	-3.749	-3.726	-3.718
		J_D	-20.679	-20.473	-20.436	-20.412	-20.405
		J_{total}	-21.080	-21.412	-21.469	-21.502	-21.515
	$^1J(\text{N}\equiv\text{C})$	J_C	10.452	9.696	9.521	9.462	9.432
		J_O	-0.779	-0.918	-0.951	-0.974	-0.982
		J_D	-15.046	-15.431	-15.149	-15.160	-15.164
		J_{total}	-5.373	-6.353	-6.579	-6.672	-6.714

triply bonded, and bears a lone pair which does not participate in the π -electron system. The same applies to analogous structures where a nitrogen atom is a part of a conjugated ring system or that of conjugated multiple bonds. In all these cases nitrogen acts as hydrogen-bond acceptors: The direction of the effects on nitrogen shielding



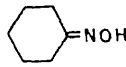
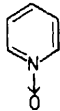
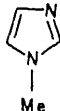
significant increase in nitrogen shielding

same as that of the analogous protonation processes (§4.2) where the proton is transferred completely to the nitrogen atoms involved to form covalent N-H bonds. Both the magnitude and direction of such hydrogen bonding effects on nitrogen shielding has recently been reproduced by quantum-mechanical calculations at a non-empirical level on imidazole (table 7) where N-3 is involved in the bonding considered above. If a nitrogen atom formally bears a lone pair which can be involved in a delocalized π -electron system, the effects of hydrogen-bonding media on the nitrogen shielding depend strongly on whether the nitrogen atom can act as a hydrogen-bond acceptor, and if so, on whether the hydrogen bonding impairs the delocalization of the lone pair over the conjugated system. Thus there is little effect on the nitrogen



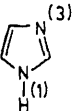
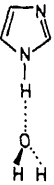
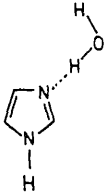
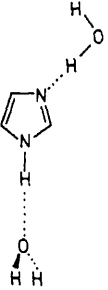
of the N-1 atom of N-methylimidazole upon changing the medium from H_2O (table 6), and the small effect observed is readily explained as that of hydrogen bonding to the N-3 atom (table 7). In contrast to this the nitrogen shielding is significantly increased in hydrogen-bonding media while N,N-dimethylaniline shows almost no effect. The delocalization of the lone pair in aniline can be obstructed by the formation of hydrogen bonds, but in N,N-dimethylaniline, steric effects exerted by the NMe_2 groups probably enforce a non-planar conformation of the NMe_2 moiety and thus obstruct the delocalization so that eventual hydrogen-bonding to the lone pair can appreciably alter the delocalization (table 6, and references therein). This is

Table 6. Hydrogen-bonding effects on nitrogen shielding.

Compound	Nitrogen shielding (in ppm, referred to neat nitromethane) for solution in solvent specified				Maximum effect observed (ppm)
	DMSO (if not stated otherwise)	MeOH	H ₂ O	CF ₃ CH ₂ OH	
	+63.1 ^a	+81.1 ^a	+84.3 ^a	+96.1 ^a	+33
PhCH=NPh	+53.7 ^b	+59.7 ^b	—	+74.0 ^c	+20
	+38.3 ^c	+50.8 ^c	—	+60.7 ^c	+22
	+86.8 ^d	—	—	+99.5 ^d	+13
Me-CN	+135.8 ^e	—	+145.0 ^f	—	+9
 (=N-) (NMe)	+125.5 ^g +221.3 ^g (in CHCl ₃)	+134.0 ^g +218.7 ^g	+134.7 ^g +217.7 ^g	— —	+9 -3
PhNH ₂	+321.3 ^h	+338.5 ⁱ	—	—	+7
PhNMe ₂	+337.2 ^j	+338.0 ⁱ	—	—	ca. 0
Me ₃ N	+368.6 ^e (neat liquid)	+363.1 ⁱ	—	—	-5
HC(=O)NMe ₂	+275.8 ^k	+272.5 ^k	+267.8 ^k	—	-8
Me ₂ NCH=CHCH=O	+293.7 ^k	+285.7 ^k	+273.2 ^k	—	-20

^a ¹⁵N data from Duthaler and Roberts 1978, recalculated according to Witanowski *et al* 1981^b Westerman *et al* 1978 details as above^c Allen and Roberts 1980, see above^d Yavari and Roberts 1979a, see above^e ¹⁴N data from Witanowski *et al* 1981, bulk susceptibility effects eliminated by using concentric spherical containers for sample and standard^f ¹⁴N data from Witanowski *et al* 1977, details as in footnote e^g Schuster and Roberts 1979, details as in footnote a^h Martin *et al* 1979, see footnote aⁱ Duthaler and Roberts 1978a, see footnote a^j Yavari and Roberts 1978c, see footnote a

Table 7. Results of *ab initio* calculations of hydrogen-bonding effects on nitrogen shielding in imidazole^a.

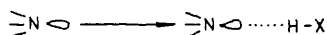
Structure	Calculated absolute shielding (in ppm)		
	For individual nitrogen atoms	Average for tautomeric equilibrium	Experimental ^b nitrogen shieldings referred to nitro-methane (in ppm)
	+181.12 (N-1) -5.66 (N-3)	+87.73	+172.6 (average) in CHCl ₃
	+173.00 (N-1) -3.99 (N-3)	+84.51	
	+177.99 (N-1) +11.92 (N-3)	+94.96	
	+171.79 (N-1) +13.94 (N-3)	+92.87	+177.2 (average) in H ₂ O

^a Prado *et al* 1981, minimal basis set, gauge-invariant atomic orbitals.

^b Schuster and Roberts, 1979; see also Witanowski *et al* 1981, p. 312.

with the direction of nitrogen shielding changes that occur upon protonation of such molecular systems in proton-donating media (§4.2).

A decrease in nitrogen shielding (*i.e.* a deshielding) is typical for situations where a nitrogen atom in a system of saturated bonds accepts hydrogen bonding *via* the lone pair or when a nitrogen atom occurs in a N-H moiety which acts as a hydrogen-bond donor (tables 6, 8 and 9). The deshielding effect on the nitrogen nucleus in an N-H



moiety which acts as a hydrogen-bond donor is reproduced by quantum-mechanical calculations for the N-1 atom in imidazole (table 7) and for the NH₂ group of formamide (table 8).

There are also some obvious examples of significant effects on nitrogen shielding when oxygen atoms, in the same molecule, are involved in hydrogen bonding as acceptors. This is the case for pyridine N-oxide (table 6) where an increase in the

Solvent	π^*	α
Cyclohexane	0.000	0.0
CCl ₄	0.294	0.0
Benzene	0.588	0.0
Pyridine	0.867	0.0
DMSO	1.000	0.0
CH ₂ Cl ₂	0.802	0.121
CHCl ₃	0.760	0.220
MeOH	0.586	0.984
H ₂ O	1.090	1.02
CF ₃ CH ₂ OH	1.018	1.51

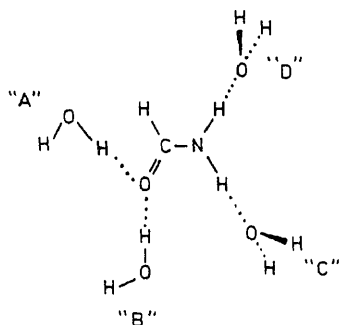
Table 8. Nitrogen shielding changes occurring upon passing from gas phase to infinitely dilute solutions (values in ppm, referred to corresponding gaseous solutes at ambient temperature, corrected for bulk susceptibility effects).

Compound Solvent	NH ₃ ^a	NMe ₃ ^a	Pyridine ^b
Cyclohexane	—	—	+1.5
CMe ₄	-13.2	-4.2	—
Benzene	—	—	+4.9
CCl ₄	-18.0	-7.3	+4.3
Me ₂ O	-9.8	-4.0	—
Et ₂ O	-12.8	-4.6	—
CHCl ₃	—	—	+12.5
CH ₂ Cl ₂	—	—	+9.1
NMe ₃	-12.1	-4.2	—
Pyridine	—	—	+6.3
NEt ₃	-14.5	-4.6	—
Me ₂ NH	-12.2	-5.0	—
MeNH ₂	-14.4	-5.1	—
Et ₂ NH	-14.8	-5.0	—
EtNH ₂	-15.7	-5.1	—
MeOH	-15.5	-9.2	+24.9
EtOH	-18.7	-8.9	—
CF ₃ CH ₂ OH	—	—	+39.9
DMSO	—	—	+6.9
NH ₃	-18.0	-5.4	—
H ₂ O	-21.5	-11.1	+28.1

^a ¹⁵N data from Alei *et al* 1970; see also Witanowski and Webb 1973, p. 247.

^b ¹⁵N data from Duthaler and Roberts 1978; see also Witanowski

in formamide^a.



Number and position of water molecules	Calculated absolute shielding for nitrogen (ppm)	Solvation shift of nitrogen (in ppm, referred to unsolvated molecule)
None	+235.99	0
1 (A)	+234.51	-1.48
1 (B)	+232.45	-3.54
1 (C)	+233.20	-2.79
1 (D)	+235.24	-0.75
2 (A+B)	+230.84	-5.15
2 (C+D)	+232.43	-3.56
4 (A+B+C+D)	+225.03	-10.96

^a Minimal basis set, gauge-invariant atomic orbitals (Prado *et al* 1981).

nitrogen shielding is observed, and for amide-type structures (table 11), where nitrogen deshielding effects are found. The latter are in agreement with the results of the theoretical calculations reported in table 9.

From the data considered, hydrogen bonding can contribute significantly to solvent effects on nitrogen shielding. It is not simple, however, to precisely determine the extent of such effects if other molecular interactions exert effects of comparable magnitude. The experimental data for pyridine shown in table 8 are rationalized in terms of two Kamlet-Taft parameters, one describing the polarity of the solvent, and another characterizing its hydrogen-bonding ability (Kollig 1979). The following values of the polarity parameter π^* (Taft and Kamlet, 1976; Kamlet *et al* 1977) and the hydrogen-bonding parameter α (derived by an analogous procedure from solvatochromic shifts in the uv-visible spectra by Kollig 1979) are used: and the following equation for the nitrogen shielding in pyridine referred to gaseous pyridine (table 8) is obtained by a least-squares fitting:

$$\Delta\sigma \text{ (solution-gas)} = 5.92 (\pi^* + 3.3\alpha) + 1.5, \quad (9)$$

with a linear correlation coefficient of 0.993 and a standard deviation of ± 1.3 ppm (Kollig 1979). Thus, about 80% of the observed range of solvent effects on pyridine nitrogen shielding is explained in terms of hydrogen bonding effects. The set of

Table 10. Liquid association shifts of nitrogen shieldings for some pure compounds at their melting points^a.

Compound	Temperature (°C)	Difference between nitrogen shielding in liquid gas phases (ppm)	Temperature coefficient of nitrogen shielding in liquid (ppm/°C)
NH ₃	-77.7	-22.6	+0.043
MeNH ₂	-93.5	-9.4	+0.016
Me ₂ NH	-96	-3.2	+0.005
Me ₃ N	-117	-6.9	+0.020
Me-CN	-45.7	+11.3	-0.021

^a Data from Alei *et al* 1971; see also Witanowski and Webb 1973, p. 253;

¹⁵N measurements, corrected for bulk susceptibility differences.

parameters used seems to be far superior to other sets, such as that of the E_T values (table 11). The use of such parameters seems to be promising in further studies, since they also show a reasonable agreement with polarity effects on the nitrogen shielding in nitroalkanes and calculations thereof in terms of the Solvaton model (§ 3). Nitrogen shieldings can be useful in the determination of the hydrogen bonding parameters α for weak hydrogen-bond donors where the solvatochromic shifts in the uv-visible spectra only provide inaccurate data.

Considerable effects of hydrogen-bonding solvents on the nitrogen shielding of amides (tables 10 and 11) are complicated not only because of the possibility of concurrent effects other than those due to hydrogen-bond formation, but also because of the fact that amides can act as hydrogen-bond acceptors, and those with NH or NH₂ moieties can act as hydrogen-bond donors to either solvent or amide molecules. Theoretical calculations (table 10) show that there are comparable effects on the nitrogen shielding of both of these processes. Factor analysis is employed to resolve the nitrogen shieldings in amides (Martin *et al* 1979; table 11) into contributions from different effects, and at least two factors are detected, one probably related to the hydrogen-bond donating properties of amides containing N-H moieties, and another which is assigned to some general property of the amide-type structure. This is not very enlightening, however, since the latter factor can contain, for example, both hydrogen-bond accepting properties (*via* the carbonyl groups) and susceptibility to bulk polarity effects. One should also be aware of the shortcomings of factor analysis and applications thereof to solvent-induced shifts in NMR spectra (Rummens 1975; p. 81).

A reasonably linear correlation between the nitrogen shielding and the E_T values of the solvents used is obtained for N,N-dimethylformamide and its vinylogues (Radeaglia *et al* 1980; table 11), but the E_T values can also contain the combined effects of bulk polarity and hydrogen-bonding.

Nevertheless, the experimental data and theoretical calculations discussed above seem to indicate that both hydrogen-bond accepting and donating by amide molecules result in a deshielding of the nitrogen nuclei involved. Thus, it is not surprising, contrary to a recent report (Hull and Kricheldorf 1980), that there is some deshielding of the nitrogen nuclei in proline-containing polypeptides upon replacing CH₂Cl₂ as solvent with a mixture of DMSO/acetone.

Table 11. Solvent effects on nitrogen shielding in amides and their vinylogues^a.

Bulk properties of solvent				Nitrogen shielding (in ppm, referred to neat nitromethane) for compound specified									
Solvent	E_T^b (kJ/mol)	Dipole moment (D)	Dielectric constant										
H ₂ O	264.1	1.8	78.5	+263.7	+263.0	+227.0	+229.7	+267.8	+273.2	+276.1	+273.4		
Ethylene glycol	235.6	2.0	37.7	+264.7	+264.9	+228.1	+231.2	+270.2	—	—	+275.8		
MeOH	232.3	1.6	32.6	+264.7	+267.4	+230.3	+232.5	+272.9	+285.7	+292.2	+278.4		
MeNO ₂	193.8	3.1	38.6	+271.1	+270.4	+232.8	+234.8	+276.5	—	—	+282.8		
Ethylene carbonate	?	4.9	89.6	+270.5	+270.1	+232.8	+234.6	+275.4	—	—	+281.8		
DMSO	188.3	3.9	48.9	+265.4	+268.9	+232.6	+234.1	+275.8	+293.7	+296.3	+282.2		
Acetone	176.6	2.8	20.4	—	—	—	—	—	+299.4	—	—		
P(NMe ₂) ₃	171.2	5.5	29.6	+266.0	+270.4	+234.2	+235.8	+278.1	—	—	+284.2		
CH ₂ Cl ₂	172.0	1.6	9.5	—	—	—	—	—	+297.3	—	—		
Cyclohexanone	170.8	2.9	18.3	+270.2	+271.2	+233.8	+235.9	+278.4	—	—	+284.6		
CHCl ₃	163.6	1.1	5.1	—	—	—	—	+275.5	+296.2	+302.5	—		
(EtOCH ₂ CH ₂) ₂ O	157.0	?	5.7	+270.2	+271.9	+234.2	+236.4	+279.4	—	—	+284.7		
Dioxan	150.7	0.4	2.2	+271.5	+271.5	+234.2	+236.2	+278.4	+301.6	—	+284.5		
Benzene	144.4	0	2.3	—	—	—	—	+280.0	+303.0	—	—		
CCl ₄	136.0	0	2.7	—	—	—	—	—	+301.8	+311.0	—		

^a ¹⁵N data from Martin *et al.* 1979 (amides) and Radeigia *et al.* 1980 (amide vinyllogues); recalculated according to Witanowski *et al.* 1981, p. 241 (residues) while the data for vinyllogues are adjusted to fit the shieldings in dimethylformamide in the former reference.

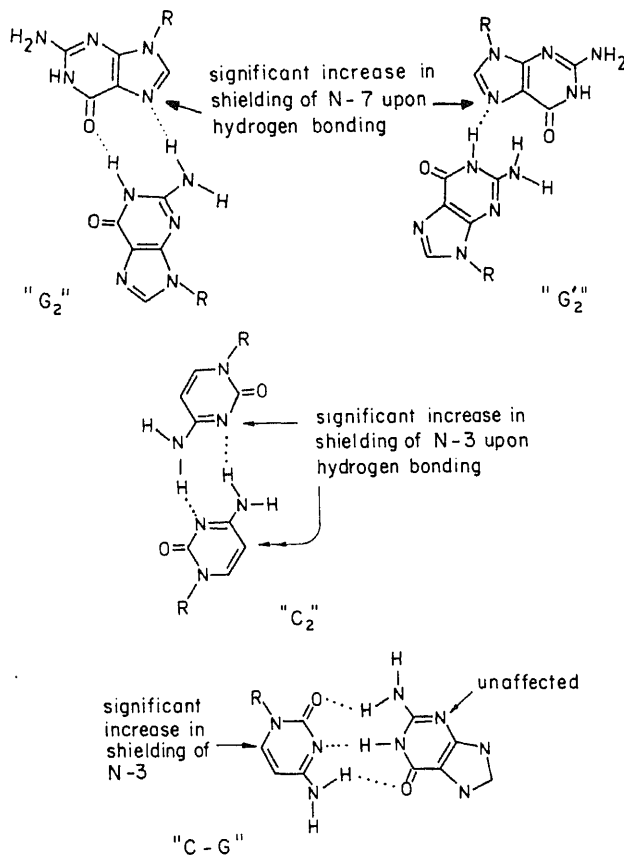
^b Solvent polarity parameter defined as solvatochromic shift in the UV spectra of a pyridinium salt in a given solvent; Dimroth and Reichardt 1969.

degree of autoassociation by hydrogen bonding of the amides both in neat liquids and in CCl_4 .

Hydrogen-bonding effects on nitrogen shieldings have been employed to estimate the secondary structure of gramicidin S, a cyclic polypeptide, the presence of four internal hydrogen bonds between amide NH groups and amide carbonyl groups are detected (Khaled *et al* 1978; Hawkes *et al* 1980). Such studies, involving the examination of solutions in DMSO and in $\text{CF}_3\text{CH}_2\text{OH}$, enable one to differentiate between solvent-exposed and solvent shielded peptide groups. Analogous studies on some linear peptides in solutions in DMSO and in H_2O reveal the usefulness of nitrogen shieldings in this differentiation (Garbay-Jauriguerry *et al* 1980).

Increasing the temperature leads to an increased nitrogen shielding in formamide, acetamide, and some derivatives thereof which is in agreement with the rupture of hydrogen bonds at elevated temperatures (Burgar *et al* 1981).

Nitrogen shielding can be employed to detect hydrogen bonding which is responsible for the so-called base pairing between purine and pyrimidine-type bases in nucleotides. Studies of this kind were carried out for uridine-adenosine systems in CDCl_3 (Poulter and Livingston 1979), and for base pairing between guanosine, cytidine, adenosine, and uridine in DMSO (Dyllick-Brenzinger *et al* 1980). The latter study suggests the following scheme of base pairing, including self-association: The study shows that adenosine in



either cytidine or guanosine.

As far as hydrogen bonding of amino groups in saturated molecules is concerned, its effect on nitrogen shielding can be obscured by other effects of the same order of magnitude. Nevertheless, there should be an appreciable contribution from hydrogen bonding to the gas-to-liquid shift of the nitrogen shieldings given in tables 8 and 10. This is shown simply by the early work of Alei *et al* 1970, since the shifts can be fitted neatly into an additivity scheme in the cases of NH_3 and NMe_3 :

$$\Delta\sigma (\text{solution-gas}) = \sum_x C_x \sigma_A(x) + \sum_y C_y \sigma_B(y), \quad (10)$$

where the σ 's are additive contributions from various active sites in solvent molecules, and the coefficients C are weighting factors, calculated as the ratio of the number of active sites concerned to the total number of active sites in a molecule of the solvent used (see also Witanowski *et al* 1973, and references therein). The following set of contributions is found to reproduce the changes in nitrogen shielding in the following table for ammonia and trimethylamine: In this manner, for example, the gas-to-

		Contribution σ to nitrogen shielding (in ppm) of solute specified	
Type of interaction		NH_3	NMe_3
Action on nitrogen lone pair electrons in solute			
Solvent OH roton	$\sigma_A(\text{OH})$	-25.2	-11.9
Solvent NH proton	$\sigma_A(\text{NH})$	-19.1	-5.4
Solvent Me group	$\sigma_A(\text{Me})$	-13.2	-4.4
Solvent Et group	$\sigma_A(\text{Et})$	-16.5	-4.7
Action on hydrogen atoms in solute			
Solvent oxygen lone-pair electrons	$\sigma_B(\text{O})$	+3.3	0
Solvent nitrogen lone-pair electrons	$\sigma_B(\text{N})$	+2.1	0

solution shift of the nitrogen shielding of NMe_3 dissolved in Et_2NH is expressed as the algebraic sum $(2/3) \sigma_A(\text{Et}) + (1/3) \sigma_A(\text{NH}) + \sigma_B(\text{N})$. Effects of hydrogen-bond accepting properties by the solute are represented by $\sigma_A(\text{OH})$ and $\sigma_A(\text{NH})$, and their direction is towards nitrogen deshielding. In contrast to this hydrogen-bond donation from solute to solvent, represented by $\sigma_B(\text{O})$ and $\sigma_B(\text{N})$, show a weak shielding effect. There are, however, considerable deshielding effects due to interactions between solutes and alkyl groups of solvents, and their magnitudes are comparable to that exerted by solvent OH and NH protons.

For neat liquid ammonia, the temperature dependence of the nitrogen shielding is tentatively explained in terms of an equilibrium between hydrogen-bonded and non-bonded molecules (Alei *et al* 1971). From the equation

$$\sigma(\text{NH}_3) = \frac{\Delta\sigma(\text{H-bond}) K_0 \exp(-\Delta H/RT)}{1 + K_0 \exp(-\Delta H/RT)} \quad (11)$$

ules and non-bonded ones, K_0 is a constant, ΔH is the enthalpy of hydrogen-bonding, and $\sigma(\text{NH}_3)$ is the observed shielding at temperature T , it is calculated that $\Delta\sigma(\text{nd}) = -24.5 \pm 0.7$ ppm.

The relatively small deshielding of the nitrogen nuclei in $^{15}\text{NH}_3$ adsorbed at type zeolites with respect to those in gaseous NH_3 , by about 3 ppm when one isolates the shift to a pore-filling factor equal to zero, is explained as a result of cancellation of the shielding effect due to hydrogen-bond donation from NH_3 to the N atoms in the zeolite system, and the deshielding effect of interactions of the lone electrons of NH_3 with the Na^+ ions and residual OH groups in the zeolite (Michel 1980). When the pore-filling factor increases, there is a further deshielding relative to the gas phase, eventually reaching that observed in neat liquid NH_3 .

The ^{15}N - ^1H couplings show effects due to hydrogen bonding of the nitrogen atom concerned with solvent molecules, as in the case of aniline derivatives (table 12). Differences in the coupling between solutions in CDCl_3 and in DMSO are suggested (Axenrod 1973) as a measure of the strength of the intramolecular hydrogen bond in substituted anilines, since in DMSO, the solute molecules are intermolecularly hydrogen-bonded to the solvent molecules.

Hydrogen bonds can also be reflected in indirectly nitrogen NMR *e.g.* from anomalous effects in tautomeric equilibria which usually lead to large changes in nitrogen shielding (§ 4.2). This is the case with histidine residues incorporated in α -lytic protease (Axenrod and Roberts 1978) where the π -H tautomer of the imidazole moiety of histidine is detected by means of its nitrogen shielding, while the τ -H tautomer usually prevails in histidine and its derivatives. The tautomeric shift to the π -H isomer

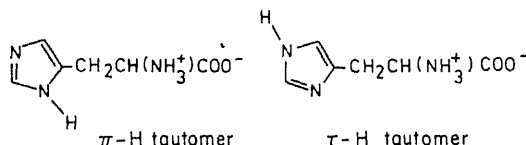


Table 12. Solvent effects on $^1J(^{15}\text{N}$ - $^1\text{H})$ of some aniline derivatives^a.

Solvent	$^1J(^{15}\text{N}$ - $^1\text{H})$ (in Hz) for aniline derivative specified						
	Unsubstituted	2-NO ₂	2-COPh	2-Cl	2-Br	2-OMe	2-F
Hexane	-78.0						
	-78.0						
	-78.6	-90.3	-88.1	-81.5	-81.4	-79.4	-80.1
	-80.6						
	-81.4						
	-82.1						
$\text{N}(\text{CD}_3)_2$	-82.3						
DMSO	-82.6	-91.0	-89.3	-84.3	-84.3	-82.3	-83.5
Difference between $\text{N}(\text{CD}_3)_2$ and DMSO							
$^1J(^{15}\text{N}$ - $^1\text{H})$ for solutions in DMSO and CDCl_3	-4.0	-0.7	-1.2	-2.9	-2.9	-2.9	-3.4

^a Data from Paolillo and Becker 1970; Axenrod and Wieder 1971; see also Axenrod 1973, in Witanowski and 1973, p. 274.

is explained in terms of hydrogen bonding between the π -NH moiety and the COO group of the aspartic acid residue, and possibly between the τ -N atom of the histidine and the OH group of the serine, since the three amino-acid residues constitute the catalytic triad of the protease.

4.2 Protonation and deprotonation processes

Protonation and deprotonation processes are important in chemistry and biochemistry, and since nitrogenous sites in molecules often play an important role in such processes, nitrogen NMR provides a powerful tool for the investigation of molecular interactions between solutes and protonating or deprotonating media. Nitrogen shieldings are frequently very sensitive to protonation-deprotonation equilibria (table 3) and the effects involved can be much larger than those from other molecular interactions.

The nitrogen shielding of amino groups usually shows some decrease upon protonation (table 13) but the effect is variable in magnitude, and sometimes leads to an increased shielding. The anomalies result from significant changes in the disposition of bonds at the nitrogen atoms involved, upon passing from an amine to the corresponding ammonium ion, when steric hindrance takes place in the molecules or, in the case of arylamines, when protonation removes the lone pair electrons on the nitrogen atom from a delocalized π -electron system. Since the effect of protonation is usually in the same direction as that due to hydrogen bonding (§4.1), estimates of changes in nitrogen shielding which result from protonation should not be made in hydrogen-bonding media.

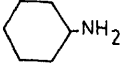
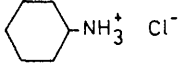
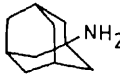
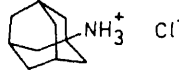
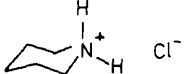
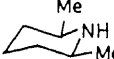
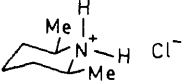
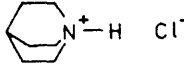
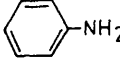
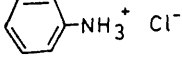
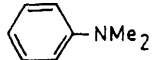
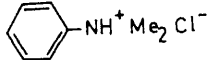
In spite of the fact that the nitrogen shielding of amino groups is less sensitive to protonation than that of other nitrogen-containing moieties, the effects are large enough to afford clear and distinct titration curves when the shieldings are recorded as a function of pH. It is possible, therefore, to quantitatively estimate the affinity of various amino groups in complicated molecules towards accepting protons (table 14) from a proton-donating medium.

The largest effects of protonation on nitrogen shieldings are observed for nitrogen atoms in multiple-bond or conjugated systems when the lone pair electrons on nitrogen are not involved in the corresponding π -electron systems (table 15). The effects are always in the direction of increased shielding, and thus they parallel those due to hydrogen-bonding (§4.1) for the structures considered, but the magnitude is much larger than that of hydrogen-bonding effects. Since the types of nitrogen atom considered occur in a number of important classes of compounds, including aromatic heterocycles, imino groups, cyano groups, and azo bridges, nitrogen shieldings are particularly useful in the detection of protonation-deprotonation equilibria in complicated molecules which contain numerous sites involved in such processes.

There are some typical examples (table 16) of strong effects on the nitrogen shielding when protonation takes place at oxygen atoms in the near vicinity of the nucleus observed in nitrogen NMR.

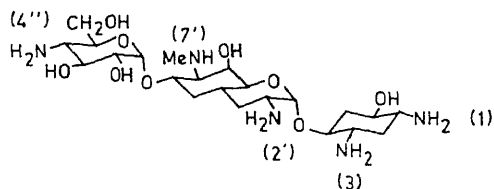
Such protonation shifts in nitrogen shieldings have been frequently employed for the investigation of molecular interactions in protonating and deprotonating media. Phenylhydrazine, PhNHNH_2 is shown to undergo protonation in CF_3COOH , mostly at the NH_2 moiety (Yavari and Roberts 1978). The nitrogen shielding of sulphonamides

Table 13. Protonation shifts for nitrogens in amino groups^a.

Parent amine	Its conjugate acid (ammonium ion)	Change in nitrogen shielding (in ppm) upon protonation in MeOH solution relative to parent amine
Alkylamines		
MeNH ₂	MeNH ₃ ⁺ Cl ⁻	-15.9
Me ₂ NH	Me ₂ NH ₂ ⁺ Cl ⁻	-12.9
Me ₃ N	Me ₃ NH ⁺ Cl ⁻	-13.4
EtNH ₂	EtNH ₃ ⁺ Cl ⁻	-8.7
<i>n</i> -PrNH ₂	<i>n</i> -PrNH ₃ ⁺ Cl ⁻	-10.6
<i>n</i> -BuNH ₂	<i>n</i> -BuNH ₃ ⁺ Cl ⁻	-10.6
<i>i</i> -PrNH ₂	<i>i</i> -PrNH ₃ ⁺ Cl ⁻	-4.1
		-5.1
<i>t</i> -BuNH ₂	<i>t</i> -BuNH ₃ ⁺ Cl ⁻	-0.6
		-0.4
(<i>i</i> -Pr) ₂ NH	(<i>i</i> -Pr) ₂ NH ₂ ⁺ Cl ⁻	+3.5
(<i>i</i> -Pr) ₂ NHMe	(<i>i</i> -Pr) ₂ NH ₂ ⁺ Me	-13.3
Alicyclic amines		
		-2.2
		+4.9
		-5.3
		-13.7
Arylamines		
		+4.1
		-7.6

^a 100 MHz, 25°C, CDCl₃. Data of Duthaler and Roberts 1978a; see also Witanowski *et al* 1981.

Table 14. Protonation-deprotonation effects on the nitrogen shieldings of apramycin antibiotic from *Streptomyces tenebrarius*^a in aqueous media.



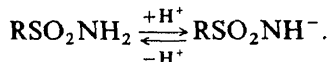
pH of 0.5 M solution in H ₂ O/D ₂ O	Nitrogen shielding referred to external neat nitromethane (in ppm) for nitrogen atom specified				
	N-1	N-3	N-2'	N-7'	N-4''
3	+ 338.1	+ 339.6	+ 338.8	+ 343.9	+ 345.3
4	+ 338.1	+ 339.5	+ 338.7	+ 343.9	+ 345.1
5	+ 338.4	+ 339.6	+ 338.7	+ 344.3	+ 345.3
6	+ 340.2	+ 339.9	+ 339.2	+ 346.7	+ 346.1
7	+ 343.4	+ 340.7	+ 340.7	+ 351.4	+ 348.8
8	+ 344.8	+ 342.9	+ 345.3	+ 354.1	+ 354.4
9	+ 346.0	+ 346.0	+ 347.4	+ 355.3	+ 356.1
10.3	+ 346.2	+ 347.1	+ 347.8	+ 355.3	+ 356.4
11	+ 346.5	+ 347.4	+ 348.3	+ 355.3	+ 356.8

pK_a values for nitrogen atoms specified, calculated from changes in nitrogen shieldings

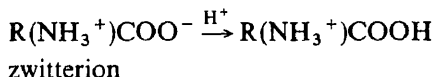
N-1	N-3	N-2'	N-7'	N-4''
6.6	8.2	7.7	6.7	7.5

^a ¹⁵N data from Dorman *et al* 1976 and Paschal and Dorman 1978 recalculated to nitromethane standard according to Witanowski *et al* 1981, p. 188.

suggesting the following deprotonation (Kricheldorf 1978):

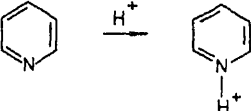
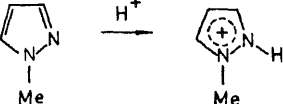
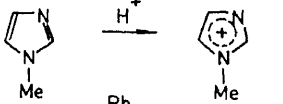
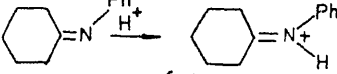
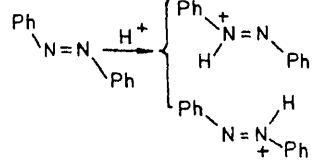
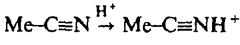


In α -amino acids, increasing acidity of the medium leads to an increase in the nitrogen shielding, but ω -amino acids do not reveal significant effects (Kricheldorf 1978). This reflects the following protonation of the acids



since the effect on the nitrogen shielding is quenched by increasing the number of carbon atoms between the NH_3^+ and COO^- moieties. Titration curves based on the observation of nitrogen shieldings in various nitrogen-containing moieties of amino acids can yield pK_a values for such moieties, as reported for histidine (Blomberg *et al* 1977; Kawano and Kyogoku 1975), arginine (Kanamori *et al* 1978; London *et al* 1978; Yavari and Roberts 1978a), and some oligopeptides (Blomberg *et al* 1978; Gatt

Table 15. Typical examples of strong effects on nitrogen shielding due to the direct protonation of nitrogen atoms^a.

Compound and its protonated form	Nitrogen shielding (in ppm, referred to external neat nitromethane) in solvent specified		Protonation shift of nitrogen (ppm)
	CF ₃ CH ₂ OH	CF ₃ COOH	
	+96.1 ^b	+184.6 ^c	+89
	+182.2 (NMe) ^d +94.4 (=N-) ^d	+186.4 (NMe) ^d +146.4 (=N-) ^d	Indirect effect, +4 +52
	+220.2 (NMe) ^e +134.0 (=N-) ^e	+217.0 (NMe) ^e +196.0 (=N-) ^e	Indirect effect, -3 +62
	+88.5 ^c	+184.1 ^c	+96
	-127.8 ^b (in isopropanol)	+22.6 ^b (in H ₂ SO ₄ /H ₂ O/EtOH)	+150
	+145.0 ^f (in H ₂ O)	+252.2 ^g (in 90% H ₂ SO ₄)	+107

^a Comparisons are made between solutions in hydrogen-bonding solvents (mostly CF₃CH₂OH) and protonating media (mostly CF₃COOH), and the values of the protonation changes in nitrogen shielding reported here are on the cautious side, since values larger by 20–30 ppm can be obtained if solutions in aprotic solvents are used as references.

^b ¹⁵N data from Duthaler and Roberts 1978, recalculated according to Witanowski *et al* 1981, pp. 335 and 390.

^c ¹⁵N data from Allen and Roberts 1980, recalculated as above, pp. 347 and 375.

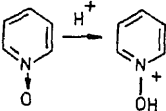
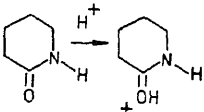
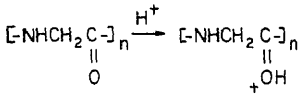
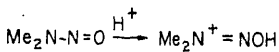
^d ¹⁵N data from Schuster *et al* 1979, recalculated as above, p. 311.

^e ¹⁵N data from Schuster and Roberts 1979, recalculated as above, p. 313.

^f ¹⁴N data from Witanowski *et al* 1977.

^g ¹⁵N data from Yavari and Roberts 1978c, recalculated as above, p. 304.

It is found that protonation effects can be employed to improve the spectral distinction of various units of polyamide polymers by means of nitrogen shielding

protonated form	solvent specified	shielding (ppm)
	$\left\{ \begin{array}{l} +99.5^b \text{ in } \text{CF}_3\text{CH}_2\text{OH} \\ +135.7^b \text{ in } \text{CF}_3\text{COOH} \end{array} \right.$	+36
	$\left\{ \begin{array}{l} +260.7^c \text{ in } \text{H}_2\text{O} \\ +243.6^c \text{ in } \text{CF}_3\text{COOH} \end{array} \right.$	-17
	$\left\{ \begin{array}{l} +276.4^d \text{ in DMSO} \\ +275.0^d \text{ in } \text{CF}_3\text{CH}_2\text{OH} \\ +271.4 \text{ in } \text{CF}_3\text{COOH} \\ +257.2^d \text{ in FSO}_3\text{H} \end{array} \right.$	-19
	$\left\{ \begin{array}{l} +148.8(\text{Me}_2\text{N}) \\ -155.4(\text{NO}) \\ +124.4(\text{Me}_2\text{N}) \\ -97.0(\text{NOH}) \end{array} \right. \left. \begin{array}{l} \text{neat liquid}^e \\ \text{in } \text{CF}_3\text{COOH}^f \end{array} \right.$	-25 +58

^a i.e. protonation of an atom other than the nitrogen atom considered.

^b ¹⁵N data from Yavari and Roberts 1979, recalculated according to Witanowski *et al* 1981 p. 357.

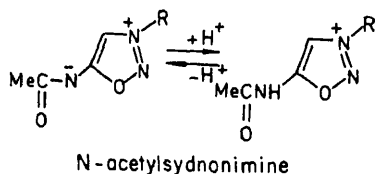
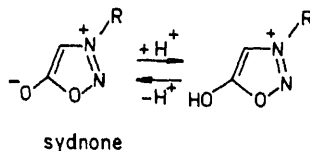
^c ¹⁵N data from Yavari and Roberts 1978, recalculated as above, p. 241.

^d ¹⁵N data from Kricheldorf 1978, recalculated as above, p. 249.

^e ¹⁴N data from Witanowski *et al* 1976.

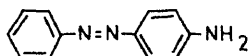
^f ¹⁵N data from Gouesnard and Martin 1979, recalculated as above, p. 396, the values are calculated for the cation from its concentration dependence of nitrogen shielding.

such as that of pyrazole and imidazole (Schuster *et al* 1979; Schuster and Roberts 1979). In sydnone ring systems, the nitrogen shieldings indicate clearly that protonation in acidic media takes place at the exocyclic moiety (Witanowski *et al* 1981; p. 83), for example. Various stages of protonation of porphyrin ring systems can be readily



observed from the corresponding changes in nitrogen shielding (Kawano *et al* 1978; Yeh *et al* 1977; Irving and Lapidot 1977).

The large shielding effect on the nitrogen nuclei which is observed upon protonation of nitrogen atoms in six-membered conjugated heterocycles (azines, *e.g.* pyridine, table 15) can be employed for the observation of protonation equilibria at various stages thereof (Witanowski *et al* 1981; p. 123, and references therein). This has been done, for example, in the case of pyrimidine and its amino-derivatives (Städeli *et al* 1980), including vitamin B₁ (Cain *et al* 1977). Analogous studies have been carried out on the protonation processes in a number of nucleosides and nucleotides (Markowski *et al* 1977; Büchner *et al* 1978; Oppenheimer and Davidson 1980). For 4-aminoazobenzene, changes in the nitrogen shielding involved indicate that with increasing acidity



of the medium employed (DMSO, DMSO + HCl, 95 % H₂SO₄), protonation takes place at the NH₂ moiety in the first stage and then a dicationic species with a protonated azo-bridge is formed (Kuroda *et al* 1980).

Spin-spin couplings between ¹⁵N and other nuclei can also provide information about protonation processes. The simplest application involves the observation of spin-spin splittings in proton-coupled ¹⁵N spectra. Since ¹⁵N-¹H couplings across one bond are large (table 17), it is straightforward to observe the formation of N-H bonds upon protonation of nitrogen atoms, provided that proton exchange with the medium is slow compared with the reciprocal of the coupling constant concerned. Such observations

Table 17. Effects of protonating media on ¹⁵N-¹H spin-spin couplings.

Solute	Solvent	Type of coupling	Value of J(Hz)
	D ₂ O	¹ J(¹⁵ N- ¹ H)	-82.6 ^a
	DCl _{aq.}	¹ J(¹⁵ N- ¹ H)	-76.0 ^b
	H ₂ O	¹ J(¹⁵ N- ¹ H)	-90.0 ^c
	CF ₃ COOH	¹ J(¹⁵ N- ¹ H)	-92.5 ^d
	H ₂ O	² J(¹⁵ N-C- ¹ H)	
		(2)CH-(1)N	-7.6 ^c
		(2)CH-(3)N	-10.8 ^c
	HCl _{aq.}	² J(¹⁵ N-C- ¹ H)	
		(2)CH-(1)N	-5.0 ^c
		(2)CH-(3)N	-5.4 ^c

^a Data from Schuster and Roberts 1980.

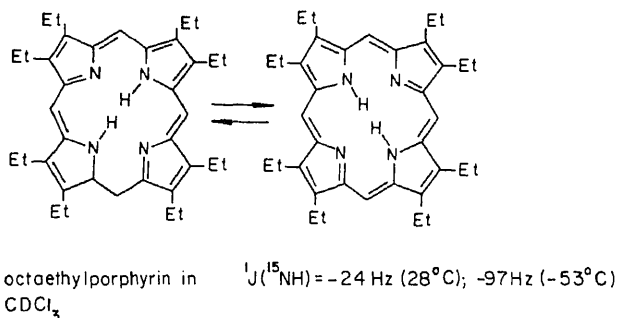
^b Data from Wasylshen 1976.

^c Data from Yavari and Roberts 1979.

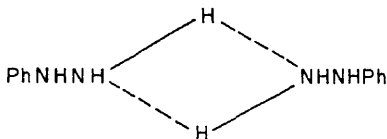
^d Data from Kricheldorf and Schilling 1978.

and direct information about the nature of the sites of protonation, and examples can be found in the literature (Witanowski *et al* 1981, and references therein) of the protonation of amines, aza-aromatic heterocycles, imines, guanidines, porphyrins, sydnonimines, and various derivatives thereof.

Rates and sites of proton exchange can be followed precisely using the information involved in the collapse of spin-spin splittings in ^{15}N spectra. There is a simple method of distinguishing between intra- and inter-molecular proton exchange. In the fast exchange limit, the former leads to weighted average couplings between ^{15}N and ^1H , while the latter results in a complete decoupling of the nuclear spins concerned. This fact has been used for the identification of internal proton migration in porphyrin systems by means of proton-coupled ^{15}N NMR spectra (Kawano *et al* 1978), since ^1H - ^{15}N NH coupling at room temperature is almost exactly 1/4 of that found at low temperatures.



Intermolecular exchange of protons leads to a collapse of spin-spin multiplet patterns resulting from ^{15}N couplings with the protons exchanged. Such dynamic changes in the ^{15}N spectra can be employed for the calculation of the rates of exchange processes. For phenylhydrazine (Yavari and Roberts 1978), PhNHNH_2 , it is found that the NH_2 protons exchange faster, by about two orders of magnitude, than the NH protons, in the neat liquid as well as in solutions in Et_3N , DMSO, CHCl_3 , EtOAc , $\text{CF}_3\text{CH}_2\text{OH}$. The fast proton exchange at NH_2 is explained in terms of formation of the dimers shown below;



where a simultaneous internal exchange can occur. Similar studies have been carried out for a number of urea derivatives (Yavari and Roberts 1980). For N-methylurea, MeNH-CO-NH_2 , the rate of exchange at NH_2 is about three times faster than in basic aqueous solutions, and about 7.5 times faster in acidic solutions. The rate of proton exchange in urea is 10 times faster than that in MeNH-CO-NHMe when the two aqueous solutions are compared, but the ratio is reduced to 1/2 in acidic solutions. While the rate of proton exchange in $\text{MeNH-CO-NHCH}_2\text{Ph}$ in basic DMSO solution is almost the same for the two NH moieties, addition of HCl increases the rate at NH_2 by about four times. A remarkable differentiation between proton exchange at NH_2 and NH is observed in MeNH-CO-NHPh since in DMSO the rate at MeNH is 50 times higher than at NH .

that at NHPH when a base is added to the solution, but the ratio changes to 1/1000 in acidic solutions. Analogous investigations on arginine (Yavari and Roberts 1978) show that the rate of exchange of protons at the δ -NH group is twice as fast as that for the terminal nitrogen atoms in the guanidino moiety. Base-catalyzed exchange rates of the protons of NH groups in a number of lactams have been determined by this method (Yavari and Roberts 1979) for aqueous and DMSO solutions; it is found that they decrease with an increase in the ring size. It has been shown (Yavari and Roberts 1978b) that 2-azacycloheptathione exchanges protons 1500 times faster than 2-azacycloheptanone.

A part from the information about protonation processes involving nuclei giving rise to multiplet patterns in ^{15}N NMR spectra, values of the couplings between ^{15}N and other nuclei, such as ^1H (table 17) and ^{13}C (table 18), can also show some characteristic trends when protonation takes place, either directly at the atom observed in nitrogen NMR or at other atoms. Such changes in the couplings can be used as indications of particular protonation mechanisms, provided that proton exchange is slow or that the coupling observed is not affected by the exchange of protons. The latter condition is fulfilled for long-range N-H couplings and carbon-nitrogen couplings.

Proton exchange processes can lead to tautomeric equilibria, and very often, when the exchange involves a nitrogen atom, the associated changes in the corresponding nitrogen shieldings are large and provide a useful tool for following solvent effects on

Table 18. Solvent effects on ^{15}N - ^{13}C couplings.

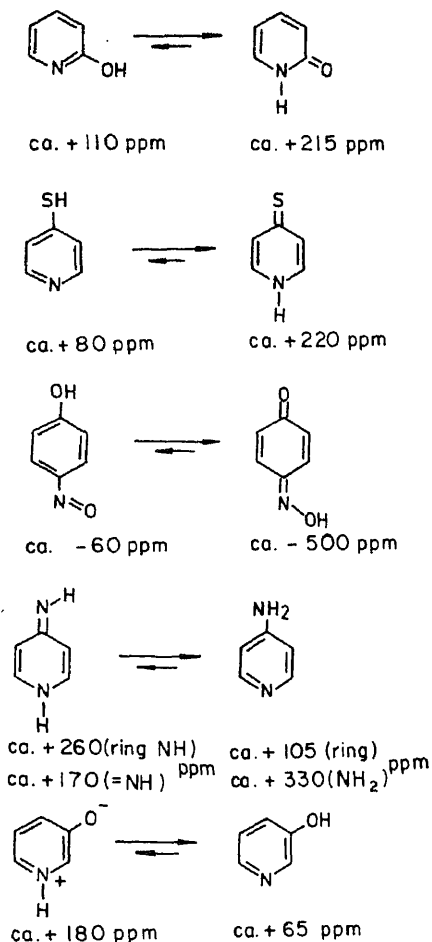
Solute	Solvent	Coupling in Hz (absolute value if not stated otherwise)		
		$^1\text{J}(\text{NC})$	$^2\text{J}(\text{NC})$	$^3\text{J}(\text{NC})$
$\text{CH}_3\text{-C(=O)-NH}_2^a$	Pyridine	14.1	8.8	
	DMSO	14.1	8.8	
	H_2O	15.5	7.3	
	CF_3COOH	18.5	3.9	
	H_2SO_4 100 %	21.0	3.4	
	FSO_3H	21.5	2.9	
Phthalimide ^a	Pyridine	12.8	?	
	DMSO	13.4	7.4	
	CF_3COOH	14.0	6.1	
	H_2SO_4 100 %	14.6	5.3	
	FSO_3H	14.6	?	
	None	10.9		
Ph-NH_2^b	DMSO	12.1		
	CF_3COOH	8.9		
	FSO_3H	8.6		
	None	10.9		
Pyridine ^c	Acetone	(+) 0.62	(+) 2.53	(-) 3.85
	MeOH/HCl	(-) 11.85	(+) 2.01	(-) 5.30
 ^d	CDCl_3	2.5	<0.3	0.3
	CDCl_3/HCl	4.0	<0.3	0.6

^a Kricheldorf 1980.

^b Axenrod *et al* 1979; Wasylishen 1976.

^c Bundgaard and Jakobsen 1976.

are given below.



In actual tautomeric equilibria, the average lifetime of at least some of the tautomers involved can be short enough to lead to dynamically averaged nitrogen shieldings which can be used as a measure of the equilibrium constant. The large differences in the nitrogen shielding between such tautomeric species make the averaged shieldings quite sensitive to changes in the equilibrium constant.

4.3 Other specific molecular interactions

Specific interactions which do not involve hydrogen-bonding or protonation can also have a significant influence on nitrogen shielding (table 3). Ion pairing effects are probably responsible for the variation of the nitrogen shielding in ammonium ions when concentrations and counterions are changed (Duthaler and Roberts 1979), as

Solvent	Concentration (mol %)	Counter-ion	Nitrogen shielding referred to neat nitromethane for $\text{MeCH}_2\text{CH}-\text{NH}_3^+$ Me (in ppm)
CHCl_3	7.3	Cl^-	+324.1
	7.3	I^-	+319.5
CF_3COOH	6.7	Cl^-	+333.2
	7.4	CF_3COO^-	+336.0
MeOH	4.0	Cl^-	+335.9
	3.8	I^-	+336.2
	4.2	CF_3COO^-	+338.3

Nitrogen shielding in NH_3 and NMe_3 (§4.1) clearly indicates that in addition to hydrogen bonding effects, there are specific interactions between solvent methyl or ethyl groups and nitrogen atoms of the solutes. The latter effects are of the same order of magnitude as those due to hydrogen bonding, and suggest the usefulness of nitrogen NMR in the investigation and detection of such non-trivial interactions.

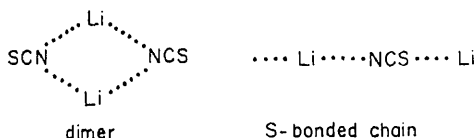
Ion association effects on nitrogen shielding can be quite large, as shown for $\text{Li}(\text{NCS})$ in table 19. The increase in shielding follows a decrease in the ionizing ability of the solvents used, in the order: dimethylformamide, tetrahydrofuran, dimethyl carbonate, diethyl ether. The dilution curves of the nitrogen shielding for $\text{Li}(\text{NCS})$ in the solvents can be explained in terms of the following equilibria:

free ions $\rightleftharpoons$ ion pairs (LiNCS in dimethylformamide)
 ion pairs $\rightleftharpoons$ dimers (LiNCS in dimethylcarbonate and ether)
 ion pairs $\rightleftharpoons$ dimers $\rightleftharpoons$ S-bonded chains (LiNCS in tetrahydrofuran)

Table 19. Examples of solvent and concentration effects on the nitrogen shielding in inorganic molecules and ions.

Solute	Solvent	Concentration	Nitrogen shielding (in ppm, referred to neat nitromethane) for species represented
$\text{K}^+(\text{NCS})^-$	H_2O	9.51 M	+170.0 ^a
	H_2O	0.30 M	+174.1 ^a
	HCONMe_2	inf. dilution	+163.2 ^b
$\text{Li}^+(\text{NCS})^-$	HCONMe_2	inf. dilution	+164 ^b
	$(\text{MeO})_2\text{CO}$	inf. dilution	+190 ^b
	tetrahydrofuran	inf. dilution	+196 ^b
	Et_2O	inf. dilution	+203 ^b
HNO_3	H_2O	1.00 M	+4.4 ^a
	H_2O	7.00 M	+12.6 ^a
	H_2O	10.00 M	+18.2 ^a
	H_2O	15.71 M (70%)	+31.1 ^a
	none	—	+47 ^c
	100% H_2SO_4	inf. dilution	+130 ^c

with the following structures for the dimers and chain polymers.



The large changes in the nitrogen shielding of HNO_3 (table 19) as its concentration in H_2O increases reflect complicated equilibria, including protonated forms, free associates, and the formation of the nitronium ion, NO_2^+ , which is revealed by a +130 ppm shielding for HNO_3 in 100% H_2SO_4 .

There have recently been some signs that nitrogen shieldings can be employed for the detection of cation binding by macrocycles that contain amido-type moieties attached to a ferrocene unit (table 20).

There is clear evidence of specific solvate formation in solutions of AgNO_3 in acetonitrile from the changes in the nitrogen shielding given in table 21. The direction of the change is consistent with the involvement in such solvates of the lone pair on the nitrogen atom in MeCN , since it is parallel to those due to other effects of the same kind, *e.g.* hydrogen bonding and protonation (§§4.1 and 4.2)

The ^{15}N spectra of the ^{15}N -labelled cyanide ions bound axially to various heme and hemoproteins (see the example in table 22 and references therein) show that the cyanide ions are exchanged with the medium since, in addition to the resonances shown in table 22, there is a signal at about +100 ppm corresponding to free cyanide ion. The large deshielding of the nitrogen nuclei in the heme-bound cyanide ions is clearly due to unpaired electron spin delocalization from the Fe(III) centre (§5), but this is significantly affected by the solvents (table 22). Thus, nitrogen shieldings are, in

Table 20. Detection of cation complexation by macrocycles with ferrocene unit by nitrogen shielding^a.

	Cation added (anion in parentheses)	Nitrogen shielding (in ppm)
	none	0 (arbitrary)
	$\text{K}^+ (\text{SCN}^-)$	0
	$\text{Li}^+ (\text{Cl}^-)$	-1.6
	$\text{Ca}^{2+} (\text{Cl}^-)$	-1.6

Table 21. Changes in the nitrogen shielding of acetonitrile upon addition of solutes^a.

Solute	Concentration (mol/kg solution)	Resulting change in nitrogen ^b shielding in MeCN relative to that for neat MeCN (ppm)
AgNO ₃	0.98	+3.4
	2.98	+9.2
	5.07	+14.5
	8.10	+20.8
Ba(ClO ₄) ₂	1.00	+2.2
	2.61	+4.9
	3.25	+5.6
AlCl ₃	0.50	+0.2
	1.18	+0.3
	2.16	+0.8

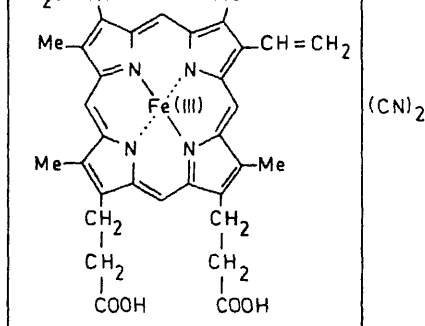
^a ¹⁵N data from Geppert *et al* 1977.^b The nitrogen shielding in neat MeCN is +135.8 ppm from neat nitromethane, see Witanowski *et al* 1981.

cases, a sensitive measure of the obstruction to spin delocalization exerted by solvent molecules.

Nitrogen shieldings have been employed as a means of determining equilibrium constants for the complexation of imidazole or N-methylimidazole with Zn²⁺ or Cd²⁺ in aqueous solutions (Alej *et al* 1978a, b, 1981). The equilibria include cations of the type Zn²⁺ (imidazole)_n or Cd²⁺ (imidazole)_n with variable *n*. It is shown that the complexation results in a considerable increase in the shielding of the N-3 atom in the imidazole system. This result can be useful in tracing the mode of binding of the metal cations to biological systems containing imidazole ring moieties.

A study of interactions between an antibody which binds trinitrophenyl groups, myeloma M315, and some trinitrophenyl 'haptens' shows that nitrogen shieldings can be used as a probe of hapten-antibody interactions (Gettins *et al* 1980). The following changes in the shielding of the nitro groups involved are observed upon binding of the haptens with the protein:

Hapten	Nitrogen shielding (in ppm) induced upon binding, referred to parent compound	
	2-NO ₂	4-NO ₂
2,4,6-trinitrotoluene	+3.3	+1.5
2,4,6-trinitroaniline	+2.1	+1.6



protohemin

Solvent	Nitrogen shielding (in ppm) for CN^- in protohemin ($\text{CN})_2$ referred to neat nitromethane
DMSO	-728
DMSO/D ₂ O (18:1)	-712
DMSO/D ₂ O (18:2)	-695
DMSO/D ₂ O (18:4)	-667
Pyridine	-692
Pyridine/D ₂ O (20:4)	-653
Pyridine/D ₂ O (20:5)	-648
Pyridine/D ₂ O (20:7)	-633
MeOD	-499
MeOD/D ₂ O (1:1)	-481
H ₂ O (pH = 9.4)	-447

* ^{15}N data for ^{15}N labelled CN^- , Morishima and Inubushi 1978, recalculated according to Witanowski *et al* 1981, p. 308.

association-dissociation effects. This has been shown for acetonitrile in solutions in CCl_4 (Tiffon *et al* 1981), where the acetonitrile ^{14}N relaxation indicates that the solute remains largely in aggregate form down to a molar fraction of 0.2, and that at lower concentrations of the solute, the aggregates begin to dissociate significantly. Similar studies have been carried out on the aggregation and de-aggregation of choline phospholipids (Murari and Baumann 1981).

5. Interactions of nitrogen with paramagnetic centres

The lone pair electrons are often the primary cause of interactions between nitrogen atoms and other species. When the interacting moiety is paramagnetic its influence on the nitrogen NMR spectrum is frequently very pronounced. Nuclear shielding, spin-spin

coupling and nuclear relaxation parameters can be profoundly changed when a paramagnetic centre is introduced. Some of these centres are specifically designed to have their major impact on the nuclear shielding-shift reagents, whereas others primarily influence relaxation phenomena-relaxation reagents.

5.1 Shift reagents

Shift reagents were initially introduced in an attempt to simplify rather complicated proton NMR spectra by inducing large shifts and thus spreading out a spectrum and effectively rendering it 'first order'. Consequently, the spectral analysis is facilitated.

The isotropic shifts produced by paramagnetic centres may arise from either, or both, of two different mechanisms (Webb 1975). One of these mechanisms produces contact interactions while the other gives rise to dipolar, or pseudo-contact, interactions between nuclear and unpaired electronic spins.

The contact shift, ΔB , at an applied field B_0 , is related to the nuclear-electron hyperfine interaction constant a_N , by

$$\frac{\Delta B}{B_0} = -\frac{a_N g_e^2 \beta_e^2 S(S+1)}{3g_N \beta_N \kappa T}, \quad (12)$$

where g_e is the rotationally averaged electronic g value, β_e is the Bohr magneton, g_N and β_N are the corresponding nuclear parameters and S denotes the spin of the unpaired electrons.

Dipolar shifts arise from the direct magnetic dipole-dipole interaction between the unpaired electronic and nuclear spins. For molecules with tetragonal symmetry the dipolar shift is given by

$$\frac{\Delta B}{B_0} = -\frac{(3\cos^2 \theta - 1)}{r^3} \frac{\beta_e^2 S(S+1)}{3\kappa T} F(g), \quad (13)$$

where r is the separation between the resonating nucleus and unpaired electrons, θ is the angle between the vector defined by r and the principal symmetry axis of the molecule and $F(g)$ is an algebraic function of the g tensor components.

Clearly (13) contains geometric information on the molecule considered whereas (12) does not. Thus although both contact and dipolar interactions can be useful in simplifying complicated NMR spectra only dipolar induced shifts can provide structural data on the species considered.

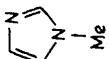
Many shift reagents operate *via* a combination of contact and dipolar interactions. Thus care has to be exercised if the induced shift is to be related to molecular structure.

Since nitrogen NMR spectra exhibit a much larger chemical shift range than that of protons, nitrogen spectra are usually well resolved and of the 'first order' type. Consequently shift reagents are rarely required to produce a simplification of nitrogen NMR spectra.

However, ambiguities can sometimes arise in the assignment of some nitrogen NMR spectra. These can often be settled by means of shift reagents such as $\text{Dy}(\text{dpm})_3$ and $\text{Dy}(\text{fod})_3$. Some examples of this are shown in table 23.

The data presented in table 23 indicate that all of the reagents considered are effective in structural differentiation at chelate to substrate molar ratios of less than 1 : 1. Thus

Table 23. Effects of some shift reagents on nitrogen shielding^a.

Solute	Solution	Nitrogen shielding (in ppm) induced by reagent specified (extrapolated to 1:1 solute/reagent ratio) referred to that in parent solution				
		Eu(dpm) ₃	Yb(dpm) ₃	Yb(fod) ₃	Dy(dpm) ₃	Dy(fod) ₃
n-PrNH ₂	$\begin{cases} 2.34 \text{ M}^b \text{ in CCl}_4 \\ 2.28 \text{ M}^c \text{ in CCl}_4 \end{cases}$	$\begin{cases} +1600 \pm 200 \\ - \end{cases}$	$\begin{cases} -340 \pm 20 \\ - \end{cases}$	$\begin{cases} - \\ - \end{cases}$	$\begin{cases} - \\ +7500 \pm 800 \end{cases}$	$\begin{cases} - \\ +6500 \pm 700 \end{cases}$
	$\begin{cases} 3.86 \text{ M}^b \text{ in CCl}_4 \\ 2.55 \text{ M}^c \text{ in CCl}_4 \end{cases}$	$\begin{cases} +1500 \pm 200 \\ - \end{cases}$	$\begin{cases} -410 \pm 20 \\ - \end{cases}$	$\begin{cases} - \\ - \end{cases}$	$\begin{cases} - \\ +7500 \pm 600 \end{cases}$	$\begin{cases} - \\ +6900 \pm 800 \end{cases}$
t-BuNH ₂	1.95 M ^c in CCl ₄	-	-	-	+3600 ± 500	+3400 ± 200
	$\begin{cases} 3.19 \text{ M}^b \text{ in CCl}_4 \\ 2.45 \text{ M}^c \text{ in CCl}_4 \end{cases}$	$\begin{cases} +1500 \pm 200 \\ - \end{cases}$	$\begin{cases} -425 \pm 20 \\ - \end{cases}$	$\begin{cases} - \\ - \end{cases}$	$\begin{cases} - \\ +4000 \pm 300 \end{cases}$	$\begin{cases} - \\ +5600 \pm 400 \end{cases}$
	$\begin{cases} 3.38 \text{ M}^b \text{ in CCl}_4 \\ (\text{N-Me}) \\ (=N-) \end{cases}$	$\begin{cases} +80 \pm 50 \\ +1400 \pm 300 \end{cases}$	$\begin{cases} -10 \pm 10 \\ -205 \pm 20 \end{cases}$	$\begin{cases} - \\ - \end{cases}$	$\begin{cases} - \\ - \end{cases}$	$\begin{cases} - \\ - \end{cases}$
	$\begin{cases} 2.63 \text{ M}^c \text{ in CCl}_4 \\ (\text{N-Me}) \\ (=N-) \end{cases}$	$\begin{cases} - \\ - \end{cases}$	$\begin{cases} - \\ - \end{cases}$	$\begin{cases} - \\ - \end{cases}$	$\begin{cases} +200 \pm 200 \\ +4000 \pm 300 \end{cases}$	$\begin{cases} +400 \pm 200 \\ +5600 \pm 400 \end{cases}$
Me-N=N ⁺ =N ⁻	$\begin{cases} 1.33 \text{ M}^c \text{ in CCl}_4 \\ (\text{Me-N=}) \\ (=N^+=) \\ (=N^-) \end{cases}$	$\begin{cases} - \\ - \\ - \end{cases}$	$\begin{cases} - \\ - \\ - \end{cases}$	$\begin{cases} - \\ - \\ - \end{cases}$	$\begin{cases} +1000 \pm 170 \\ +200 \pm 40 \\ +90 \pm 70 \end{cases}$	$\begin{cases} +1300 \pm 400 \\ +160 \pm 20 \\ 0 \pm 80 \end{cases}$
Me-N=C=O	2.97 M ^c in CCl ₄	-	-	-	+70 ± 120	0 ± 100

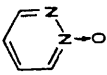
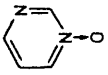
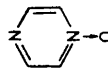
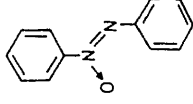
$\text{Me-N}=\text{C}=\text{S}$	2.95 M ^c in CCl_4	—	—	—	0 ± 110	0 ± 60
Me-CN	3.08 M ^b in CCl_4	—	—	—	—	—
	3.91 M ^c in CCl_4	—	—	—	+ 1200 ± 400	+ 3000 ± 600
HCONMe_2	2.22 M ^b in CCl_4	+ 50 ± 30	—	—	—	—
	2.77 M ^c in CCl_4	—	—	—	+ 250 ± 200	100 ± 200
MeNO_2	neat liquid ^{b,c}	0 ± 10	0 ± 10	—	0 ± 10	0 ± 10
	{ in CHCl_3 ^d (=N-) (N → O) }	—	—	—	—	—
		—	—	-86 -119	—	—
	{ in CHCl_3 ^d (=N-) (N → O) }	—	—	+5 -32	—	—
		—	—	—	—	—
	{ in CHCl_3 ^d (=N-) (N → O) }	—	—	—	—	—
		—	—	-77 -86	—	—
	{ in CHCl_3 ^d (=N-) (N → O) }	—	—	—	—	—
		—	—	-28 -44	—	—

Table 23. (Continued)

Nitrogen shielding (in ppm) induced by reagent specified (extrapolated to 1:1 solute/reagent ratio) referred to that in parent solution						
Solute	Solution	Eu(dpm) ₃	Yb(dpm) ₃	Yb(fod) ₃	Dy(dpm) ₃	Dy(fod) ₃
PhCH ₂ OCO-Gly-Leu-Leu-OMe 0.5 M in CH ₂ Cl ₂ ^c	(Gly)	+66	—	—	—	+294
	(Leu)	+78	—	—	—	+312
	(Leu-OMe)	+66	—	—	—	+222
PhCH ₂ OCO-Ala-Leu-Leu-OMe 0.5 M in CH ₂ Cl ₂ ^c	(Ala)	—	—	—	—	+288
	(Leu)	—	—	—	—	+270
	(Leu-OMe)	—	—	—	—	+270

^a dpm = (Me₃C-CO-)₂CH⁻; fod = CF₃CF₂-CO-CH⁻-CO-CMe₃.^b ¹⁴N data, referenced to internal nitromethane standard; see Witanowski *et al* 1971b and also Witanowski and Webb 1973, p. 254.^c ¹⁴N data, referenced to internal nitromethane standard; see Witanowski *et al* 1973.^d ¹⁵N data, referred to an external standard, uncorrected for bulk susceptibility effects; see Städeli *et al* 1980 and also Witanowski *et al* 1981, p. 148.^e ¹⁵N data, details as in footnote d; Kricheldorf and Hull 1980; Gly = glycine residue, Ala = alanine residue, Leu = leucine residue.

For example the nitrogen shielding of the isocyano group lies within the range characteristic of alkylamines but the response of the isocyano nitrogen to the shift reagents is very small, whereas that of alkylamines is very large. Thus any uncertainty between isocyanide and alkylamine resonances can be removed in the presence of the shift reagents. A similar differentiation is possible between the pyrrole-type and the pyridine-type of nitrogen nuclei in azoles where the characteristic ranges of nitrogen shielding overlap to a significant degree.

With a view to investigating the possibility of using shift reagents to obtain structural data from nitrogen NMR spectra, various lanthanide reagents have been added to pyridine, various amines and other nitrogen-containing substrates (Witanowski *et al* 1971a, b). As shown in table 24, at a 1 : 1 chelate to pyridine ratio substantial nitrogen shielding changes are induced by the paramagnetic lanthanide (dpm)₃ chelates. By comparison with the theoretical estimates of unpaired spin density (Golding and Halton 1972) it appears that the induced nitrogen shifts are dominated by a contact interaction this being particularly true for the reagents Gd (dpm)₃ and Dy (dpm)₃. Thus most of the shift reagents considered in table 24 are unsuitable for obtaining geometrical data from nitrogen NMR spectra. It seems likely that nitrogen NMR spectra will, in general, exhibit induced shifts due to a substantial contact interaction.

5.2 Relaxation reagents

In principle, relaxation reagents may operate through three possible mechanisms (Hexem *et al* 1976). The simplest interaction gives rise to outer sphere relaxation which envisages no chemical interaction between the substrate and the paramagnetic centre.

Table 24. Comparison of nitrogen shielding induced by lanthanide (dpm)₃ chelates in pyridine with theoretical calculations of unpaired electron spin density on lanthanide ions^a.

Ion	Configuration	Calculated unpaired spin density term	Nitrogen shielding (in ppm) induced by the corresponding lanthanide (dpm) ₃ chelate in ca. 2.5 M solutions of pyridine in CCl ₄ , extrapolated to 1 : 1 chelate/pyridine molar ratio
La ³⁺	<i>f</i> ⁰	0	-380 ± 30
Ce ³⁺	<i>f</i> ¹	+0.979	-290 ± 50
Pr ³⁺	<i>f</i> ²	+1.967	-450 ± 300
Nd ³⁺	<i>f</i> ³	+2.685	-360 ± 300
Pm ³⁺	<i>f</i> ⁴	+1.618	Data not available
Sm ³⁺	<i>f</i> ⁵	+1.184	-540 ± 50
Eu ³⁺	<i>f</i> ⁶	-10.682	+1500 ± 200
Gd ³⁺	<i>f</i> ⁷	-31.500	+2900 ± 500
Tb ³⁺	<i>f</i> ⁸	-31.818	Data not available
Dy ³⁺	<i>f</i> ⁹	-28.545	+4000 ± 300
Ho ³⁺	<i>f</i> ¹⁰	-19.954	+2100 ± 200
Er ³⁺	<i>f</i> ¹¹	-13.349	+870 ± 100
Tm ³⁺	<i>f</i> ¹²	-7.049	Data not available
Yb ³⁺	<i>f</i> ¹³	-2.587	-425 ± 20

^a dpm = (Me₃C-CO)₂CH⁻; calculations from Golding and Halton 1972, experimental data from Golding *et al* 1971, Witanowski and Webb 1973, p. 255.

In this case the relaxation mechanism is spin-dipolar interaction between the nuclear and unpaired electronic spins modulated by translational diffusion. The corresponding nuclear relaxation time, T_1 , is given by

$$\frac{1}{T_1} = \frac{16S(S+1)}{15\hbar^2\kappa T} g_N^2 \beta_N^2 g_e^2 \beta_e^2 \pi^2 \eta N, \quad (14)$$

where N is the number of paramagnetic centres per unit volume of solution and η is the viscosity of the solution.

If the substrate becomes bound to a paramagnetic relaxation reagent then the second mechanism, which is spin-dipolar interaction modulated by rotational reorientation of the resulting bound complex, may be operative in producing nuclear relaxation. Under these circumstances the relaxation rate, T_1^{-1} , is given by

$$\frac{1}{T_1} = \frac{2S(S+1)g_N^2\beta_N^2g_e^2\beta_e^2}{15\hbar^2r^6} \left[\frac{3\tau_c}{1+w_N^2\tau_c^2} + \frac{7\tau_c}{1+w_e^2\tau_c^2} \right], \quad (15)$$

where r is the separation between the nucleus of interest and the paramagnetic centre, w_N and w_e are the nuclear and electronic Larmor frequencies from which it follows that $w_e \gg w_N$ which is a necessary precondition for the derivation of equation (15).

The correlation time, τ_c , for the bound complex depends upon τ_R , the corresponding rotational correlation time, τ_M , the mean lifetime of the nucleus of interest in the bound state and the electron spin relaxation time, τ_s , as shown by (16).

$$\frac{1}{\tau_c} = \frac{1}{\tau_R} + \frac{1}{\tau_M} + \frac{1}{\tau_s}. \quad (16)$$

Since nitrogen nuclei, when present, usually form the binding site for the substrate-relaxation reagent complex then r in (15), becomes reasonably small such that nitrogen relaxation rates are normally determined by (15).

For nuclei which are further from the binding site, (14) may be more important as, indeed, may be the third relaxation reagent mechanism. This is scalar interaction modulated by rotational reorientation of the bound complex. In this instance the relaxation rate is given by,

$$\frac{1}{T_1} = \frac{2S(S+1)a_N^2}{3\hbar^2} \left[\frac{\tau_e}{1+w_e^2\tau_e^2} \right], \quad (17)$$

where the correlation time, τ_e , is obtained from (18)

$$\frac{1}{\tau_e} = \frac{1}{\tau_s} + \frac{1}{\tau_M}. \quad (18)$$

Since $w_e^2\tau_e^2$ is very large, (17) only becomes important as a relaxation mechanism when a_N is large. However, the corresponding influence on the relaxation time T_2 is considerably greater as shown by (19)

$$\frac{1}{T_2} = \frac{S(S+1)}{3\hbar^2} a_N^2 \left[\tau_e + \frac{\tau_e}{1+w_e^2\tau_e^2} \right]. \quad (19)$$

Thus, in the general case, NMR linewidths are likely to be severely influenced by means of the effect of a bound paramagnetic centre on T_2 , as shown by (19) or by means of T_1 as

The gadolinium relaxation reagents $\text{Gd}(\text{dpm})_3$ and $\text{Gd}(\text{acac})_3$, have been employed for studies on ^{15}N relaxation (Levy *et al* 1978). In the presence of $5 \times 10^{-4} \text{ M Gd}(\text{dpm})_3$ the basic nitrogen nuclei of imidazole show an increase in relaxation rate from 0.13 S^{-1} to 1.83 S^{-1} whereas the corresponding change for N methyl formamide is from 0.043 S^{-1} to 0.048 S^{-1} . These data suggest direct bonding between gadolinium and the basic imidazole nuclei, whereas in N methyl formamide bonding may occur with the carbonyl oxygen atom. Thus relaxation reagents may be used as spin-labels for molecules containing both basic and non-basic nitrogen sites.

The relaxation reagent $\text{Cr}(\text{acac})_3$ is fairly kinetically inert and thus its relaxation function most probably arises through the outer sphere mechanism described by (14). It is often assumed that such an interaction may produce nuclear relaxation without significantly influencing the corresponding nuclear shielding. However, caution is necessary in making such assumptions. As shown in table 2 an increase occurs in the nitrogen shielding of pyridine by about 0.4 ppm at a molar ratio of $\text{Cr}(\text{acac})_3$ to pyridine of 1:100 (Witanowski *et al* 1981).

The fact that the relaxation reagent, $\text{Gd}(\text{dpm})_3$ forms complexes due to nitrogen coordination is borne out by the results presented in table 2. The shielding increase of almost 7 ppm noted for the pyridine nitrogen is strongly indicative of coordination with the added relaxation reagent. For neat pyridine the corresponding nitrogen shielding increase, due to the addition of $\text{Gd}(\text{dpm})_3$, is about 3500 ppm. By using a constant concentration of $0.01 \text{ M Gd}(\text{dpm})_3$ the maximum induced nitrogen shielding of pyridine occurs at about 3 M. Hence concentrations of $\text{Gd}(\text{dpm})_3$ of 10^{-4} or greater produce significant shielding increases for sterically accessible nitrogen atoms.

5.3 Complex formation

It is well known that nitrogenous compounds form good ligands for transition metal ions. The most common form of coordination interaction between the ligand and the metal ion is donation of a lone pair of electrons from the nitrogen to the metal ion. If the metal is paramagnetic then the shielding of the donating nitrogen atom is strongly influenced by the unpaired electrons. The change in nitrogen shielding may arise from the contact interaction, equation (12), or the dipolar interaction, equation (13).

In studies of the ^1H NMR spectra of ligands attached to a paramagnetic transition metal ion a_N , from (12), is usually expressed by

$$a_N = QI/2S, \quad (20)$$

where S refers to the unpaired electron spin in the molecule, I is the unpaired spin density on the atom to which the proton is attached, for π delocalisation of spin $Q = -2.25 \text{ mT}$ and for σ delocalisation $Q = 50.8 \text{ mT}$. The smaller value of Q for π delocalisation reflects the relative inefficiency of the less direct spin polarisation mechanism compared to σ electron delocalisation. The opposite signs of Q suggest that σ and π electron transfers should produce induced shifts in opposite directions. However, although the spin density I usually has the same sign for each proton when σ delocalisation occurs for π delocalisation I can take alternating signs throughout the conjugated system. Hence σ electron transfer results in large shifts in the same direction for each proton site on the ligand whereas T_1 electron transfer produces somewhat smaller shifts, as a rule with alternating signs.

and σ electron processes with paramagnetic metal ions, provided that the observed shifts are dominated by the contact interaction.

For the same amount of S electron spin density, nitrogen-induced contact shifts are about twice as large as those for carbon and about fifteen times as large as those for protons (Goodman and Raynor 1970). Consequently nitrogen shielding changes due to complex formation with a paramagnetic transition metal ion, are very likely to be dominated by the contact interaction and may thus usefully provide information on the electron transfer processes occurring. La Mar and Walker (1979) have provided an interesting account of the analysis of the spin distribution in paramagnetic porphyrins from NMR data.

Shifts of about 1000 ppm are observed for the nitrogen nucleus in cyano complexes of Cr, Mn, Fe, Co and Ni, these correspond to a positive spin density on the nitrogen (Shporer *et al* 1965). Morishima and Inubushi (1978) have used ^{15}N labelled cyanide in order to study the influence of axially bound ligands to the ferric ion in porphyrin derivatives and some hemoproteins such as cytochrome C and some myoglobins. Nitrogen-induced shifts from 500 to 1200 ppm are observed which are very solvent-sensitive but are not dependent upon substitution of the porphyrin peripheral groups. If one of the two axial cyanide ligands is replaced by various pyridines the nitrogen shielding of the remaining cyanide decreases significantly as the basicity, of the particular pyridine chosen, increases. From these observations it seems likely that the decrease in cyanide nitrogen shielding in passing from the cytochrome C to the myoglobin cyanide results from a change in the effective strength of proximal histidine binding to the heme iron atom rather than from structural changes in the heme peripheral groups.

Since the induced nitrogen shifts, due to coordination with a paramagnetic ion, are rather large it follows that they may be used to study weak interactions such as those arising from solvation and ion pairing and ligand exchange processes (Webb 1975; Orrell 1979). In the case of acetonitrile exchange with various paramagnetic transition metal ions, ^{14}N NMR data reveal rate constants varying between $2.1 \pm 0.3 \times 10^3 \text{ S}^{-1}$ for Ni(II) and $1.2 \pm 0.3 \times 10^7 \text{ S}^{-1}$ for Mn(II).

Thus the interactions produced concomitantly with ligand complexation to a paramagnetic metal ion can be usefully monitored by means of nitrogen NMR.

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Studies of ion-molecule interactions by NMR spectroscopy

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1. Introduction

The subject matter of this paper received a powerful new impetus in the 1970s with the advent of Fourier-transform spectrometers which rendered possible the *direct* study of less-receptive nuclei, including metal ion nuclei often endowed with an electric quadrupole moment: approximately three out of four nuclei in the periodic table are quadrupolar. Because of this technological breakthrough, we shall restrict our coverage to these more recent studies, which have provided a wealth of information about ion-molecule interactions. This report will be even more biased; it will focus mostly on *cation*-molecule interactions, simply because these have been studied much more, and for a variety of reasons—specific cation complexants, such as crown ethers and cryptands, have been very much in the center of attention since the first report by Pedersen in 1967—than *anion*-molecule interactions. To venture a rough estimate, the literature about ion-molecule interactions studied by NMR consists to the extent of $\approx 80\%$ of publications on cation-molecule interactions, and of $\approx 20\%$ of papers about anion-molecule interactions. Also, and for the obvious reason of greater familiarity, our examples will be somewhat slanted towards systems which have been studied in our laboratories at Liège and Ottawa. We deliberately omit consideration of the simplest ion, the proton H^+ , because there has been a large number of NMR studies of protonation equilibria, including some very fine reviews.

There are basically two ways to consider and subdivide the subject of ion-molecule interactions (tables 1 and 2). In order to keep this paper reasonably concise and to avoid

Table 1. Subdivision on the basis of molecular type and size.

A_1	Ion-solvent and/or ion-other small organic molecules
B_1	Ion-biomolecule, with one or a small number of binding sites
C_1	Ion-polyelectrolyte

Table 2. Subdivision based upon the features of the ion-molecule interaction.

A_2	Stoichiometry	C_2	Geometry
B_2	Thermodynamics	D_2	Kinetics and microdynamics

classification, based upon molecular type, rather than upon the latter, more methodological scheme of table 2. We shall introduce the methodology (A_2 , B_2 , C_2 , D_2) as we go along; our paper is problem-oriented rather than method-oriented. However, we shall strive to emphasize those aspects of the results which make nuclear magnetic resonance invaluable and probably the *most powerful method presently available for studying ion-molecule interactions in solutions*.

2. Ion-solvent interactions

NMR methods are unique for study of ionic solvation, because they provide a *local* picture. In most cases, the NMR spectrum for the ion itself, or for nuclei in solvent molecules, is affected predominantly by nearest neighbour interactions. In other terms, NMR 'sees' the coordination shell around an ion: the various NMR parameters, *i.e.* the chemical shift, or chemical shifts if several lines coexists, their relative intensities, the relaxation rates for the various nuclei, can be and have been related to the composition of this *first* solvation shell (throughout this section, we shall use interchangeably the two equivalent terms of coordination shell (or sphere) and first solvation shell (or sphere)).

The first question is that of the number of distinguishable chemical entities within this coordination sphere. Coordination numbers (or equivalently solvation numbers) can be determined by NMR. Not only can they be determined, but in certain cases, under conditions of slow exchange, *i.e.* for kinetically inert complexes, the determination is unambiguous.

The second type of problem relates to exchange between free ligands in the bulk solvent and bound ligands on the ionic center. The kinetics can be followed, and they discriminate clearly between *associative* and *dissociative* mechanisms.

Thirdly, if one uses a binary mixture of two solvents A and B, the composition of the first solvation sphere can differ markedly from that of the bulk solvent. We shall describe various powerful formalisms for quantitative analysis of such *preferential solvation*.

Fourthly, even in a pure solvent A, a given ion is surrounded not necessarily only by A molecules since its counterion can also penetrate the coordination shell: we shall describe examples of such mixed solvation-counterion complexes.

Finally, if to first approximation the first solvation sphere around a given ion does not include the counterion, it may become possible to relate empirically the NMR observables for the ion to macroscopic or microscopic solvent properties, such as viscosity, polarity, hydrogen-bond donor strength, electron donor strength, etc.

2.1 Solvation number

Let us start with a concrete example, that of the trimethylphosphate (TMPA) solvate of aluminum-III perchlorate in nitromethane solution (figure 1a) (Delpuech *et al* 1975). The ^{27}Al ($I = 5/2$) spectrum consists of a heptet of lines, with the binomial distribution 1 : 6 : 15 : 20 : 15 : 6 : 1. This indicates a structure in which all ligands are fully equivalent, arranged at the six corners of an octahedron centred on the metal, to which they are bonded through oxygen $\text{P}=\text{O} \dots \text{Al}$, the ^{31}P - ^{27}Al scalar coupling constant (figure 1) being close to 20 Hz. One should note that the octahedral symmetry of the AlA_6^{3+}

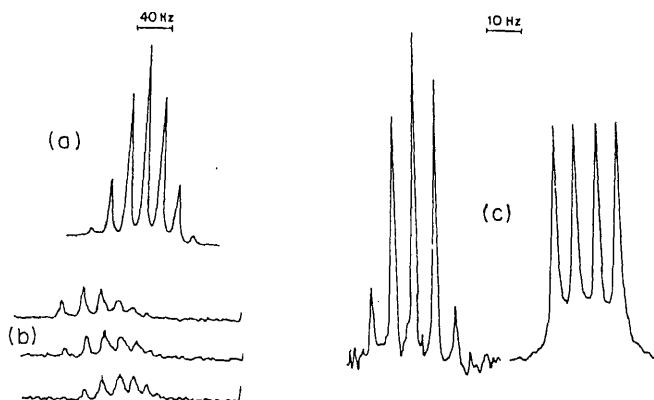


Figure 1. (a) ^{27}Al NMR spectrum of a nitromethane solution of $\text{Al}(\text{TMPA})_6^{3+}$, 3ClO_4^- at 25°C (from Delpuech *et al* 1975); (b) ^{27}Al NMR spectra of 0.013 molal $\text{Al}(\text{ClO}_4)_3$ solutions in mixtures of DMF and DMSO in nitromethane ($X_{\text{DMF}} = 1 - X_{\text{DMSO}} = 0.3, 0.4, 0.5$) (from Schneider 1976); (c) ^9Be (left) and ^{31}P (right) NMR spectra of $\text{Be}(\text{HMPT})_2^{2+}$, 2ClO_4^- in nitromethane (from Delpuech *et al* 1977).

species ($\text{A} = \text{TMPA}$) is characteristic of an instantaneous O_h structure, and not a time-averaged composite between structures having lower symmetries: ^{27}Al has a quadrupolar nucleus ($Q = 0.149 \times 10^{-24} \text{ cm}^2$); if the symmetry of the AlA_6^{3+} entity had deviated significantly from full octahedral symmetry, it would have resulted in a non-vanishing electrostatic field gradient q at the aluminum nucleus, whose interaction with the nuclear quadrupole moment Q would have led to efficient quadrupolar relaxation, translating into very broad lines which, most probably, would have rendered impossible detection of the ^{27}Al resonance, let alone resolution of the scalar couplings to the six phosphorous nuclei. Equivalently, the ^{31}P spectrum for the same AlA_6^{3+} solvate ($\text{A} = \text{TMPA}$) shows six lines with equal intensities, corresponding to the $\pm 5/2$, $\pm 3/2$, and $\pm 1/2$ spin states of the aluminum nucleus.

The two point symmetry groups leading to a vanishing electrostatic field gradient for ML_n^{m+} complexes, in which all the ligands L are identical, are the O_h and the T_d . For aluminum solvates, while trialkylphosphates, phosphonates, dialkyl hydrogen phosphites give rise to octahedral AlA_6^{3+} species, the hexamethylphosphoric triamide solvate is a tetrahedral AlA_4^{3+} species.

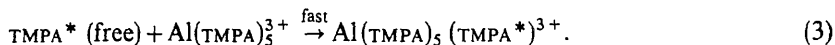
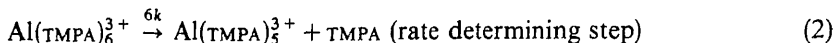
Such determinations of the solvation number are totally unambiguous, and not fraught with the uncertainties associated with other methods. To give just two more examples, out of the prolific literature, the solvation number of $\text{Al}(\text{III})$ by dimethylsulphoxide (DMSO)-dimethyl formamide (DMF) mixtures, in nitromethane solution, is 6 (Schneider 1976) (figure 1b) and the solvation number of $\text{Be}(\text{II})$ by TMPA, by dimethylphosphonate, by N,N -dimethylamido- O,O' -dimethylphosphate, by *bis*(N,N -dimethylamido)- O -methylphosphate, and by HMPT, is 4 (Delpuech *et al* 1977) (figure 1c).

2.2 Solvent exchange kinetics

Consider the process,

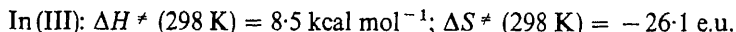
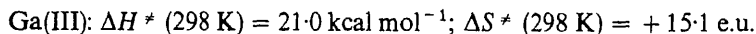
Two limiting mechanisms have been distinguished (Langford and Gray 1966): in the *associative* ('S_N2-type') mechanism, the coordination number of the transition state (or intermediate) is *greater* by one unit to that of the initial or final state; in the *dissociative* ('S_N1-type') mechanism, the coordination number of the transition state (or intermediate) is *smaller* by one unit to that of the initial or final state.

Octahedral aluminum (III) complexes, such as that formed with TMPA, have been found to undergo solvent exchange by a dissociative mechanism, according to the following equations:



The rate constant, k , is indeed independent of the concentration of the *free* TMPA ligand (Delpuech *et al* 1975). By contrast, tetracoordinate aluminum-III complexes, such as that with HMPT, have been found by the same authors to obey an *associative* substitution mechanism, with a bimolecular rate law (first-order in free ligand). This mechanistic change, it was reported in the same study (Delpuech *et al* 1975), is accompanied by a strong decrease of the activation enthalpies and entropies; $\Delta H^\ddagger$ (298 K) = 23.5 (TMPA) and 7.7 (HMPT) kcal mol⁻¹; $\Delta S^\ddagger$ (298 K) = +18.2 (TMPA) and -10.2 (HMPT) e.u. These spectacular changes are nicely consistent with the switch in mechanism.

The substitution mechanism is dissociative for $\text{Ge}(\text{TMPA})_6^{3+}$ and associative for $\text{In}(\text{TMPA})_6^{3+}$, with the following Eyring activation enthalpies and entropies:



(Rödehüser *et al* 1977).

For the tetrahedral beryllium-II solvates, studied in nitromethane solution, again, as with aluminum-III, the substitution mechanism is a sensitive function of the ligand type: associative with TMPA ligands ($\Delta H^\ddagger$ = 13.4 kcal mol⁻¹; $\Delta S^\ddagger$ = -12.9 e.u.), and dissociative with HMPT ligands ($\Delta H^\ddagger$ = 27.9 kcal mol⁻¹; $\Delta S^\ddagger$ = +18.7 e.u.). This was ascribed by the authors to steric overcrowding of a pentacoordinate (associative) transition state with the bulky HMPT ligand (Delpuech *et al* 1977).

Additional information, allowing even more secure distinction between associative and dissociative mechanisms for solvent exchange on a cationic center, is provided by precise determinations of volumes of activation as effected in recent years, especially by the group of Prof. Merbach in Lausanne (see, for instance, Swaddle and Merbach 1981). His findings are consonant with those reported above: in general, for labile octahedral complexes, a dissociative mechanism applies; this is the case for $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$. Surprisingly, the process is associative with $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, both at atmospheric and at high pressures (Swaddle and Merbach 1981).

2.3 Preferential solvation

When a mixture of two solvents dissolves a salt, the two solvents will compete to occupy

coordinated solvent molecules will be also 0.5. The two mole ratios will differ if one of the two solvents is more efficient in occupying the coordination sites of the cation. One can, in this way, define a qualitative solvating ability. The quantitative definition is in the determination of the equilibrium constant for replacement of one solvent molecule by another.

Just like in the determination of the coordination number (see §2.1), it is possible with kinetically inert solvates to obtain precise and detailed information on the ratios of the different solvates in equilibrium. This is, for example, the case of the solvation of Al^{3+} by binary mixtures of DMSO and DMF (figure 2), where one can distinguish the six different solvates of composition $[\text{Al}(\text{DMSO})_z(\text{DMF})_{6-z}]^{3+}$, where $z = 1, 2 \dots 6$ and one could calculate accurately the different equilibrium constants K_i ($i = 1-6$) corresponding to the equilibria of (1), simply by integration (eventually after deconvolution) of the different lines:

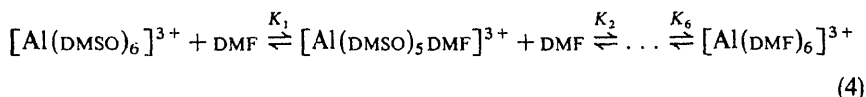


Figure 2 permits also a direct qualitative description of the system with regard to preferential solvation: in the case of a nonpreferential competition, at a molar ratio of 0.5, the system of multiplets should be symmetrical, the two central lines being of equal intensity. In the case of figure 2, this is achieved for $X_{\text{DMF}} = 1 - X_{\text{DMSO}} \simeq 0.8$, showing a preferential solvation of Al^{3+} by DMSO. Incidentally, one should mention the quasi ideal additivity of the chemical shifts of the different solvates.

Delpuech *et al* (1971) have determined in this manner the successive equilibrium constants for Al^{3+} and Be^{2+} in aqueous mixtures of organophosphorous solvents, and

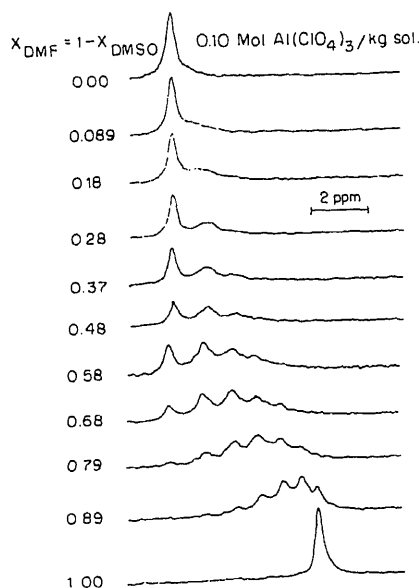


Figure 2. ^{27}Al NMR spectra of 0.10 molar $\text{Al}(\text{ClO}_4)_3$ solutions in mixtures of DMF and DMSO

Sheppard 1967) or $\text{Mg}(\text{ClO}_4)_2\text{-H}_2\text{O-Acetone}$ (Ioma *et al* 1973).

The problem is much less readily solved when all solvates are in rapid chemical exchange. This is generally the case for an alkali cation in a mixture of aqueous or non-aqueous solvents: the observables, chemical shift and linewidth, vary regularly between the two characteristic values for each solvent (figure 3), as is exemplified for the case of the sodium cation dissolved in binary mixtures of some amines and tetrahydrofuran (THF) (Delville *et al* 1981a).

Qualitatively, the curvature can be interpreted by preferential solvation. Thus, Bloor and Kidd (1968) have shown that sodium ions are preferentially solvated by water in the binary mixture water/acetonitrile, in view of the curvature of the graph of ^{23}Na chemical shift with molar fraction. Frankle *et al* (1970) have proposed a qualitative measure of this preference, as the value of the molar fraction corresponding to the algebraic mean of the chemical shifts in the two pure solvents: they called this point the isosolvation point. One can directly see in figure 2 that the solvating ability of amines in competition with THF towards the sodium cation is decreasing in the order: propylamine > isopropylamine > pyrrolidine > piperidine $\approx$ pyridine > aniline. In the same way, it has been possible to rank numerous non-aqueous solvents as a function of their ability to solvate the sodium cation in binary mixtures (Erllich *et al* 1973; Greenberg and Popov 1975).

Our approach to preferential solvation has been to consider *jointly* the chemical shift and the relaxation rate, which are the two observable parameters (Detellier and Laszlo 1976). We have developed a model based on application of the Hill formalism (Hill 1910), widely used in biochemical studies of phenomena such as cooperative oxygen binding to hemoglobin (Gill *et al* 1978). Mathematically, preferential solvation of a tetracoordinated ion, and binding of a ligand to one of four equivalent sites in a

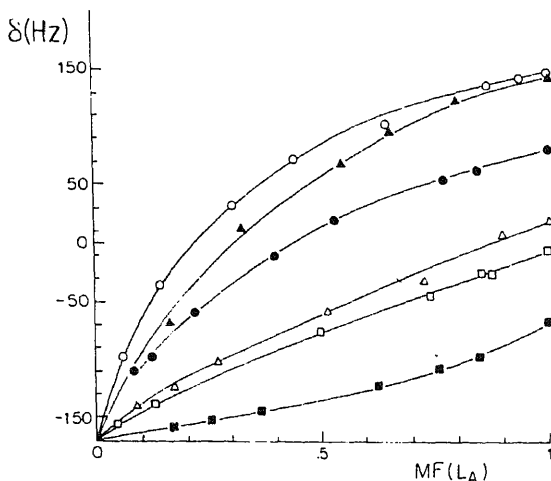
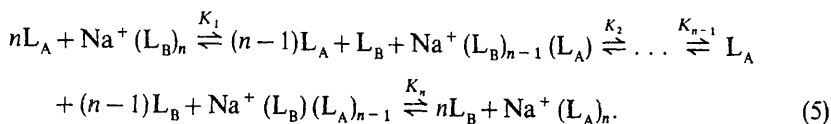


Figure 3. Variation of the ^{23}Na chemical shift δ against mole fraction of the amine, from the binary mixtures of aniline (■), pyridine (□), piperidine (◻), pyrrolidine (◻), propylamine (○), and iso-propylamine (▲), with THF (from Delville *et al* 1981a).

biomolecule, constitute one and the same problem (Delville *et al* 1980, 1981a). If the two components of a binary solvent mixture which compete for solvation of the Na^+ cation share the same solvation number n , $(n+1)$ complexes can be formed in succession, related by the following series of successive equilibria (5).



Inserting the relevant statistical factors leads to the *intrinsic* equilibrium constants k_i , defined from the relation,

$$k_i = \frac{n-i+1}{i} K_i. \quad (6)$$

In the case of the tetracoordination ($n=4$), a most likely case for the sodium cation in non-aqueous or aqueous solvents (Van Geet 1972; Michaelian and Muscovits 1978), (7) is obtained (Delville *et al* 1981a),

$$Y = \sum_{i=1}^4 \frac{i\alpha_i}{4} = \sum_{i=1}^4 \frac{i\beta_i X^i}{4D}, \quad (7)$$

where Y is the fraction of sites on the Na^+ cation occupied by a ligand L_A , $X = [\text{L}_A]/[\text{L}_B]$, $D = \sum_{i=0}^4 \beta_i X^i$; $\beta_0 = 1$, $\beta_i = K_1 \dots K_i$, and $\alpha_i = \beta_i \frac{X^i}{D}$.

A *Hill* plot is a representation of $\ln(Y/1-Y)$ as a function of $\ln X$ (figure 4). In the case of equality of all these intrinsic constants, *i.e.* under the absence of cooperativity, the *Hill* plot becomes linear with a unit slope, and one obtains,

$$\ln \frac{Y}{1-Y} = \ln K + \ln X. \quad (8)$$

The *Hill* plots on figure 4 have been produced by a calculation of Y , the saturation fraction, from the chemical shifts:

$$(\delta_{\text{obs}} - \delta_0) = \sum_{i=1}^4 \alpha_i (\delta_i - \delta_0) \quad (9)$$

where δ_i is the chemical shift of the i th species, the $\text{Na}^+(\text{L}_B)_{4-i}(\text{L}_A)_i$ solvate. Introducing the standard assumption of additive chemical shifts, an assumption that we have tested (Delville *et al* 1981c),

$$Y = (\delta_{\text{obs}} - \delta_0)/(\delta_4 - \delta_0). \quad (10)$$

For all the unidentate ligands studied the *Hill* plots are linear, with unit slope, and yield directly the intrinsic solvation constant k (table 3).

It may be noted that (8) is identical with previous equations reported in the literature based on models for preferential solvation, with the assumption of equality of each intrinsic equilibrium constant (Covington *et al* 1973) or, in the case of a non-statistical distribution, with introduction of an adjustable parameter (Covington and Thain 1974). Thus preferential solvation data have been derived from Covington's statistical

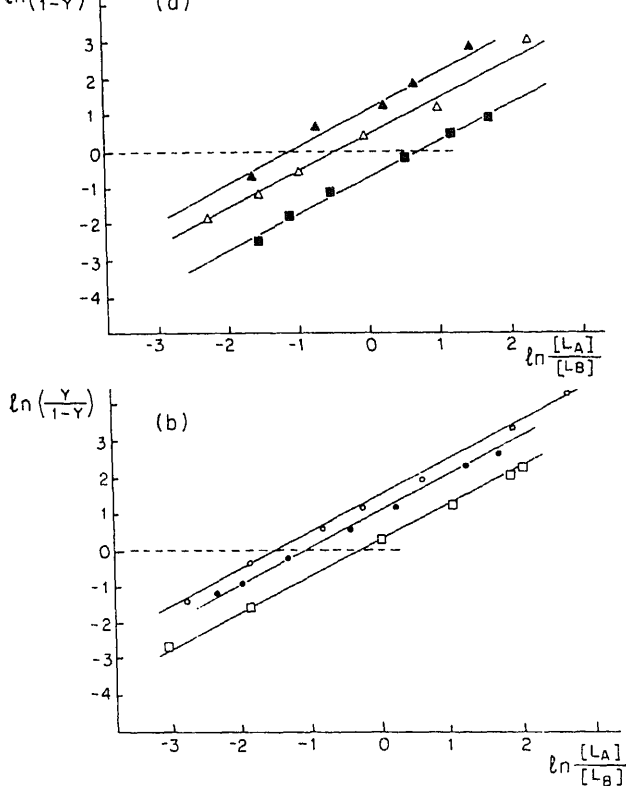


Figure 4. Hill plots for the binary mixtures of (a) aniline (■), piperidine (△), isopropylamine (▲) (b) pyridine (□), pyrrolidine (●), propylamine (○) and THF (from Delville *et al* 1981a).

the thallium cation (Briggs and Hinton 1979; Covington and Newman 1979).

We have extended the application of the Hill formalism to the case of polydentate ligands in competition with THF. Figure 5 shows the variation of the chemical shifts of Na-23 in binary mixtures of polyamines (ethylenediamine, diaminopropane, cadaverine) and THF. The curvature is very pronounced, showing a strong preferential solvation by the polyamines, as was the case for previous studies with diethylenetriamine (Detellier *et al* 1979).

The analysis of the data is based on the following model (Delville *et al* 1981b):

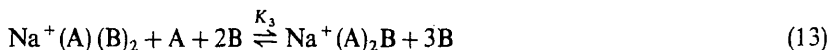
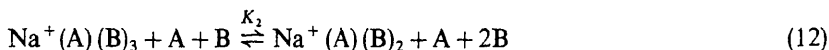
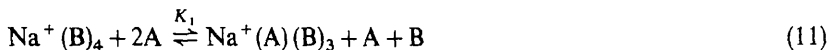


Table 3. Slope of the Hill plots (the linear correlation coefficients are above 0.996 for at least 6 points), values of the intrinsic equilibrium constants; and chemical shifts for $^{23}\text{Na}^+ \text{ClO}_4^-$ (10^{-2} M) in each solvent measured with respect to aqueous NaCl solution extrapolated to infinite dilution (Delville *et al* 1981).

Solvent	δ_4 (ppm)	Slope of the Hill plot	Intrinsic constant k
Aniline ($\text{C}_6\text{H}_5\text{NH}_2$)	-3.39	1.00	0.46
Pyridine ($\text{C}_5\text{H}_5\text{N}$)	-0.45	0.96	1.3
Piperidine ($\text{C}_5\text{H}_{10}\text{NH}$)	0.89	1.03	1.5
Pyrrolidine ($\text{C}_4\text{H}_8\text{NH}$)	3.67	0.96	2.8
<i>i</i> -Propylamine ($i\text{-C}_3\text{H}_7\text{NH}_2$)	6.80	1.12	3.0
Propylamine ($\text{C}_3\text{H}_7\text{NH}_2$)	6.73	0.97	4.4

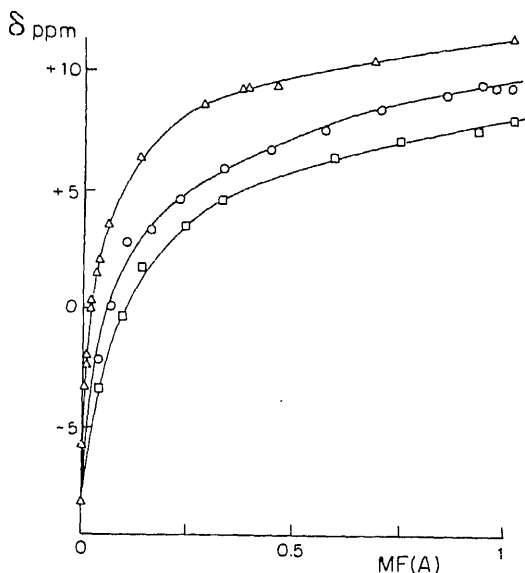


Figure 5. Variation of the ^{23}Na chemical shift δ against mole fraction of the polyamine for the binary mixtures of cadaverine ($\square$), diaminopropane ($\circ$) and ethylenediamine ($\triangle$) with THF (from Delville *et al* 1981b).

One obtains the saturation fraction $Y/(1 - Y)$:

$$Y/(1 - Y) = \frac{\beta_1 X + 2\beta_2 X(R_A X + R_B) + 3\beta_3 X^2(R_A X + R_B) + 4\beta_4 X^2(R_A X + R_B)^2}{4 + 3\beta_1 X + 2\beta_2 X(R_A X + R_B) + \beta_3 X^2(R_A X + R_B)} \quad (15)$$

from the values of table 4, the entries of the first and second diamine molecules into the sodium coordination shell are independent and equiprobable steps: $k_1 = k_3$ and $k_2 = k_4$. This permits also a direct determination of the chelate effect, defined as the ratio of complexes having bidentate attachment of the ligand to the metal, to the complexes in which only unidentate binding occurs: hence the chelate effect is measured by the quantities α_2/α_1 , or α_4/α_3 . Values of 4.5 (cadaverine), 8.0 (1,3-diaminopropane) and 12.0 (ethylenediamine) are found.

2.4 Mixed solvent-counterion complexes

After having considered, in the previous section, competition between solvent molecules for metal ion coordination, we turn now to the related case of competition between solvent molecules and counterions for attachment to an ionic center. A number of interesting studies have considered competition between acetonitrile solvent molecules and halide anions for coordination to aluminum-III (Dalibart *et al* 1981; Wehrli and Hoerdts 1981; Wehrli and Wehrli 1981). Solutions of AlCl_3 or AlBr_3 in the high dielectric ($\epsilon = 38.8$) acetonitrile have good electrical conductivity, which suggests the presence of ionic species. The nature of these ionic species has been examined by various methods during the last decade, with rather inconclusive results (Hon 1968; Haraguchi and Fujiwara 1969; Akitt and Duncan 1977; Beattie *et al* 1979; Akitt *et al* 1979). More recent studies taking advantage of modern-high field NMR spectrometers have provided 'unequivocal evidence for a whole range of mixed complexes involving both the counterion and solvent molecules as ligands' (Wehrli and Wehrli 1981).

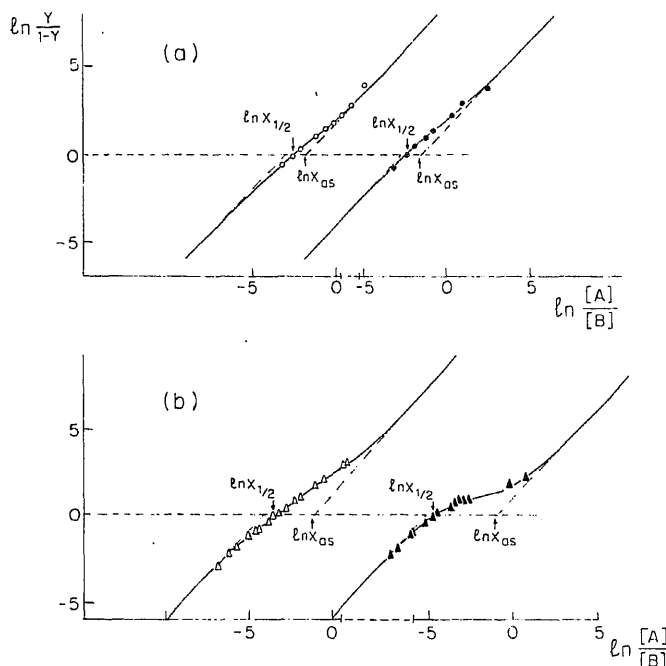


Figure 6. Hill plots for each of the system of figure 5, plus diethylenediamine ($\blacktriangle$) (from Delville *et al* 1981b).

Table 4. Values of the intrinsic equilibrium constants (k) for the successive replacement of THF molecules by amine solvents.

Solvent	k_1	$k_1 k_2$	k_3	$k_3 k_4$
CDV ^a	0.9	20	1.1	43
DAP	0.4	38	0.5	35
EDA	1.5	110	1.1	95

^aCadaverin (CDV), 1,3-diaminopropane (DAP) and ethylenediamine (EDA) (Delville *et al* 1980).

For instance, when AlI_3 is dissolved in acetonitrile, only AlA_6^{3+} ($\text{A} = \text{CH}_3\text{CN}$) and AlI_4^- can be detected (Wehrli and Wehrli 1981). With AlBr_3 , under similar conditions, besides the tetrahedral AlBr_4^- anion, AlA_6^{3+} , $\text{AlA}_5\text{Br}^{2+}$, and AlA_4X_2^+ (*cis*) coexist in the solution: the composite broad resonance observed for ^{27}Al at 23.45 MHz with $\delta \approx -30$ ($\text{Al}(\text{H}_2\text{O})_6^{3+}$ was used as the reference) was quantitatively analyzed to yield the relative concentrations of the three cationic species, which were identified from their individual ionic charge (Dalibart *et al* 1981). Higher field ^{27}Al spectra (at 78.2 and 93.8 MHz) fully confirmed this identification, by resolving the individual lines (Wehrli and Wehrli 1981). With aluminium chloride, besides the AlCl_4^- peak, individual resonances were detected for the given coexisting species (table 5). This is a rather spectacular experiment, since all but one of the possible 10 complexes were resolved. Likewise since addition of small amounts of water consecutively displaces chloride ions and acetonitrile from the coordination sphere, nine out of ten theoretically possible mixed solvates of stoichiometry $[\text{AlA}_n(\text{H}_2\text{O})_{6-n}]^{3+}$ were also identified in this study (Wehrli and Wehrli 1981).

Identification of the ^{27}Al lines was based, in the work we have just referred to, on the concentration dependence of the spectrum for AlCl_3 in acetonitrile, and on the progressive deshielding of the ^{27}Al nucleus as chlorine replaces nitrogen in a stepwise manner, and the net charge goes from +3 to -3. Also, the ^{27}Al linewidths, being proportional to the mean square of the electrostatic field gradient at the nucleus, are very sensitive to it. As can be seen from the following table 6, a simple point charge calculation (Valiev and Zaripov 1966) predicts vanishing field gradients, not only for the two O_h molecules AlA_6^{3+} and AlCl_6^{3-} , but also for the C_{3v} *fac* isomer AlA_3Cl_3 (*cis*): accordingly these three species give rise to sharp ^{27}Al resonances.

We have focused on these AlX_3 -acetonitrile systems as a nice illustrative case in which nearly all of the possible solvates could be observed. A number of related studies have been performed for other Lewis acids under various conditions—to give just two examples: the chemical shift of ^{67}Zn reflects the formation of chloride and bromide complexes (Maciel *et al* 1977); likewise the ^{113}Cd chemical shift can be used to monitor the distribution of Cd^{2+} , CdI^+ , CdI_2 , CdI_3^- , and CdI_4^{2-} species in H_2O and DMSO

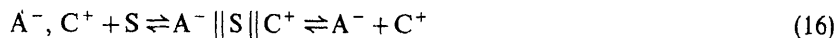
Species	δ , ppm from $\text{Al}(\text{H}_2\text{O})_6^{3+}$
AlA_6^{3+}	-32.6
$\text{AlA}_5\text{Cl}^{2+}$	-21.6
$\text{AlA}_4\text{Cl}_2^+$ <i>cis</i>	-14.3
$\text{AlA}_4\text{Cl}_2^+$ <i>trans</i>	-12.3
AlA_3Cl_3 <i>cis</i>	-7.5
AlA_3Cl_3 <i>trans</i>	-6.2
$\text{AlA}_2\text{Cl}_4^-$ <i>cis</i> or <i>trans</i>	-1.2
$\text{AlA}\text{Cl}_5^{2-}$	+2.8
AlCl_6^{3-}	+7.4

Table 6. Electric field gradient tensor invariant $\langle e^2q^2 \rangle$.

Complex (symmetry group)	$\langle e^2q^2 \rangle$
$\text{MX}_6 (O_h)$	0
$\text{MX}_5\text{Y} (C_{4v})$	$9(e_2/r_2^3 - e_1/r_1^3)^2$
<i>trans</i> - $\text{MX}_4\text{Y}_2 (D_{4h})$	$36(e_2/r_2^3 - e_1/r_1^3)^2$
<i>cis</i> - $\text{MX}_4\text{Y}_2 (C_{2v})$	$16(e_2/r_2^3 - e_1/r_1^3)^2$
<i>trans</i> - $\text{MX}_3\text{Y}_3 (C_{2v})$	$27(e_2/r_2^3 - e_1/r_1^3)^2$
<i>cis</i> - $\text{MX}_3\text{Y}_3 (C_{3v})$	0
<i>trans</i> - $\text{MX}_2\text{Y}_4 (D_{4h})$	$36(e_2/r_2^3 - e_1/r_1^3)^2$
<i>cis</i> - $\text{MX}_2\text{Y}_4 (C_{2v})$	$16(e_2/r_2^3 - e_1/r_1^3)^2$
$\text{MXY}_5 (C_{4v})$	$9(e_2/r_2^3 - e_1/r_1^3)^2$
$\text{MXY}_6 (O_h)$	0

Calculated for the central atom in octahedral complexes $\text{MX}_n\text{Y}_{6-n}$ assuming interatomic distances r_1 and r_2 for the metal-ligand bonds and ligand charges e_1 and e_2 , (Valiev and Zaripov 1966).

formed in reactions. The equilibrium involved is the following (A^- = anion; C^+ = cation; S = solvent molecule(s)):



ion pair: intimate loose dissociated
 contact solvent-
 tight separated

Such an equilibrium can be followed by nuclear magnetic resonance since the observables, especially the chemical shift is (or can be) very sensitive to the inter-ionic distance. Examples studied include that of sodium iodide, which exists predominantly as the tight ion pair in THF and as a loose ion pair in diglyme or triglyme (Detellier and Laszlo 1975a), while sodium perchlorate exists as the loose ion pair in all these oxygenated solvents.

Two sorts of experimental situations, if set up, should be distinguished. Either one is looking at a series of solvents in direct interaction with the ion; or intervening ligands, or a cage formed by a neutral molecule such as a crown ether or a cryptand, shield the ion from direct contact with solvent molecules.

Clearly, the former case appears as the only possibility for measuring parameters such as the internal pressure, to take an almost purely 'physical' interaction, or the amount of electron transfer from solvent molecules to the ion, an example of a more 'chemical' phenomenon. Such determinations, however, will be fraught with problems coming from the coexistence of several factors. Suppose that we wish to determine the aptitude of solvents to serve as electron-donors towards univalent cations M^+ , and that we use for this purpose the chemical shift for an appropriate nuclide M : it may well be that this observable will depend *also* upon, for instance, the internal pressure. In which case, since the series of solvents ($S_1, S_2, S_3, \dots S_i$) whose electron-donor properties we want to determine will have variable internal pressures p_i , the determination won't be extremely clean. We shall refer below to such determinations as *experiments of the first type*. The other possibility is to immerse the ion in a molecular framework protecting it from direct contact with solvent molecules so that, for instance, variable electrostriction of solvent molecules around the ion will be suppressed or at least greatly reduced. Then it should be possible to gain access to solvent parameters in a less straightforward manner but more cleanly. We shall refer to such set-ups as *experiments of the second type*.

2.5a Experiments of the first type: For a quadrupolar nucleus, under extreme narrowing conditions, the longitudinal and transverse relaxation rates are equal and proportional to the square of the electrostatic field gradient at the nucleus, multiplied by a correlation time τ_c :

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{3\pi^2}{10} \frac{2I+3}{I^2(2I-1)} \left(1 + \frac{\eta^2}{3}\right) \left(\frac{e^2 q Q}{h}\right)^2 \tau_c. \quad (17)$$

When, to first approximation, the only variable is τ_c , the relaxation rates are often found to reflect the local viscosity (or microviscosity) determining τ_c , according to a suitable modified Debye-Stokes-Einstein (DSE) relation (Gierer and Wirtz 1953):

$$\tau_c \equiv \tau_R = \frac{V\eta}{KT} \rightarrow \tau_R \frac{a_{\text{solute}} \cdot V_{\text{solute}}}{a_{\text{solvent}} \cdot 6kT} \cdot \eta, \quad (18)$$

where a is a molecular radius, and V the molecular volume. Hence, one may find very simply that the relaxation rates T_1^{-1}, T_2^{-1} (or equivalently the linewidth $\Delta\nu_{1/2}$ since $T_2 = (\pi\Delta\nu_{1/2})^{-1}$) are linear with respect to the bulk viscosity η . Such a finding has been reported for $^{23}\text{Na}^+$ ($I = 3/2$) in a series of eight solvents (Detellier and Laszlo 1975):

$$\tau_c = 0.74\eta + 1.31. \quad (19)$$

Or conversely, by using a series of solvents varying relatively little in viscosity, one may find that the relaxation rate is affected principally by changes in the electrostatic field gradient from the chemical ion-solvent molecules interaction. For instance, it was reported that the $^{23}\text{Na}^+$ linewidth is approximately linear with respect

$$T_1^{-1}(\text{Hz}) = 7.6 \text{ DN} - 89.$$

But the ^{23}Na chemical shift provides a more reliable measure of the donor strength: Popov (1975) found a very nice inverse linear correlation between the infinite dilution ^{23}Na chemical shift for Na^+ and the Gutmann donor number (DN) (Gutmann 1978) in 16 solvents. Similar correlations were later reported for $^{39}\text{K}^+$ and $^{133}\text{Cs}^+$ by the group at Michigan State (De Witte *et al* 1976; Shih and Popov 1977), as indicated in table 7.

2.5b Experiments of the second type: Such determinations are much more promising and, even though there are presently relatively few examples of these, we venture the guess that these should grow rapidly in the future.

When the complex formed between the Na^+ cation and the dibenzo-24-crown-8 is studied in solution, the geometry of the complex and thereby the magnitude of the ^{23}Na quadrupolar coupling constant remain invariant to very good first approximation, because the sodium ion is secluded away by the crown ether from contact with the solvent (figure 7). Thus, in acetone-pyridine mixtures, the linewidth is nicely linear in the bulk viscosity, varying between *ca* 40 and 120 Hz as the viscosity goes from 0.34 to 0.95 cP, with very little scatter (Bisnaire *et al* 1982). The ^{59}Co nucleus has an exquisitely broad range of chemical shifts, of the order of 20,000 ppm, because the cobalt atom has low-lying excited states, so that the paramagnetic part of the shielding constant, in the Ramsey formalism, is extremely sensitive to tiny perturbations in *d-d* transitions. Many diamagnetic low-spin cobalt (III) complexes are known. However, because of the large magnitude of the quadrupole moment *Q* of the cobalt nucleus, only highly symmetrical complexes such as CoL_6 will give rise to sharp NMR lines. An example is $\text{Co}(\text{CN})_6^{3-}$, in which the six equivalent cyanide ligands shelter the metallic center from oxidizing solvent molecules. Cobalt hexacyanide is thus a perfectly stable entity. It has been used to probe a series of solvents, *S*, according to their electron-acceptor strength: $\text{Co}-\text{L}:\ddot{\text{S}}$.

The ^{59}Co chemical shift is nicely linear with respect to the Gutmann acceptor number AN (Gutmann 1978) ($\rho = 0.98$ for 27 different solvents; Laszlo and Stockis 1980). In the same study, the authors also reported on the use of the cobalt (III) hexacyanide probe to measure the hydrogen-bonding donor ability of protic solvents HS, according to the scheme: $\text{Co}-\text{L}:\ddot{\text{H}}\ddot{\text{S}}$. The reciprocal δ^{-1} of the ^{59}Co chemical shift is linear with the difference between the density of cohesive energy D_{ce} and the internal

Table 7. Chemical shifts (ppm) at infinite dilution for $^{23}\text{Na}^+$, $^{39}\text{K}^+$, and $^{133}\text{Cs}^+$ in various solvents.

Solvent (DN)	Na^+	K^+	Cs^+
Nitromethane (2.7)	-15.6	-21.10	-59.8
Acetonitrile (14.1)	-7.0	-0.41	+32.0
Dimethylsulphoxide (29.8)	-0.11	+7.77	+68.0
Propylene carbonate (15.1)	-9.4	-11.48	-35.2
Methanol (27.5)	-3.8	-10.05	-45.2
Dimethyl formamide (26.6)	-5.0	-2.77	-0.5
Acetone (17.0)	-8.4	-10.48	-26.8
Pyridine (33.1)	1.35	0.82	-31.0

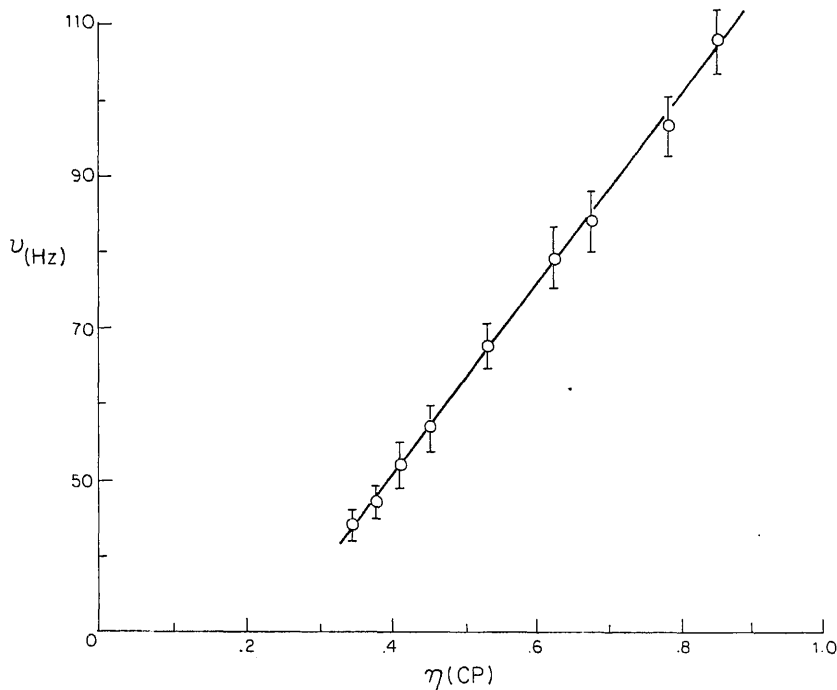


Figure 7. ^{23}Na NMR signal half height linewidths (ν) against viscosity (η) for the complex sodium perchlorate—DB24C8 dissolved in binary mixtures of acetone and pyridine ($P = 0.999$ for 10 points).

pressure P_i , which measures the density of hydrogen bonding (Reichardt 1979) in 10 different solvents (Laszlo and Stockis 1980).

3. Interactions between ions and small organic molecules

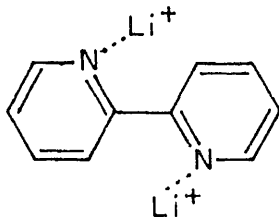
In §2.3, we have examined the situation in which two neutral solvent molecules A and B compete for the same ion. This is very similar to having an ion dissolved in a solvent A and capable of binding another solute B. We shall examine now such ion-solute complexes, focussing mostly on these cases in which the solvent A interacts only weakly, with the ion studied by comparison to the strength of the interaction between the ion and B.

We shall term B a *ligand* molecule, and we shall consider in turn *acyclic ligands* (3.1), *monocyclic ligands* (3.2), and *polycyclic ligands* (3.3). By ‘cycle’ we mean, not necessarily a ring in the usual sense (atomic connectivity), but a cavity-containing topology. To give an example, the molecule of dibenzo-24-crown-8 referred to earlier (in §2.5b) will be considered as a *monocyclic ligand* for the purpose of this section.

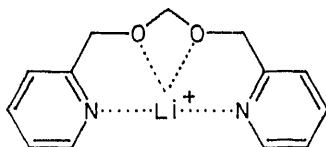
3.1 Acyclic ligands

The case of polyamines has been treated above (in §2.3), and we have also referred to the

The interaction of alkali ions with 2,2'-bipyridine, using ^7Li , ^{23}Na , ^{39}K , ^{133}Cs and ^{13}C NMR, was studied in several non-aqueous solvents (Schmidt *et al* 1981). While the good electron-donors, tetrahydrofuran, methanol, and dimethylformamide solvate Li^+ quite effectively, in the poorer donor propylene carbonate and, especially, in nitromethane, 2,2'-bipyridine is able to compete effectively with solvent molecules for coordination to the cation. From the plot of the ^7Li chemical shift as a function of ligand-to-lithium mole ratio, Schmidt *et al* were able to conclude the formation of the 2:1 lithium-2,2'-bipyridine complex: This conclusion was confirmed, in nitromethane

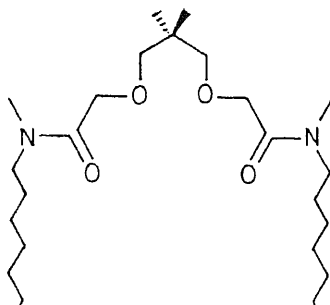


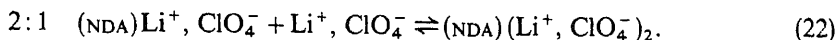
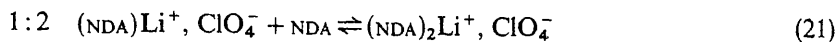
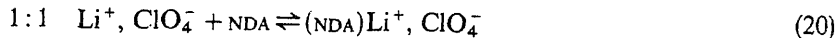
solution, by examination of the titration curves for the various carbon-13 nuclei of the ligand molecule (Schmidt *et al* 1981). Another *bis*-pyridinic ligand has been studied by the Liège group, using ^7Li and ^{23}Na , in nitromethane solution. There, the stoichiometry is definitely 1:1, as indicated by the structure (Cornéls *et al* 1982): Both these ligands complex alkali metal ions in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+$.



Once the stoichiometry of an ion-molecule complex is established through continuous variation of their molar ratio, one can proceed to determine the formation constant of the complex, and the attendant ΔH^0 and ΔS^0 variations.

The complexation of lithium ions with acyclic polydentate amido ethers was investigated by ^1H and ^7Li NMR in various solvents (Olsher *et al* 1980). The ligands used were the tetradentate $\text{N,N}'$ -diheptyl- $\text{N,N}',5,5'$ -tetramethyl-3,7-dioxanonanedi-*amido* (NDA) and the bidentate N -methylheptyl-3-oxapentanamide (PMA): NDA is superior to PMA in complexing lithium ions. Various types of complexes can form and coexist:





Their presence, as well as the magnitude of the formation constants K , depend markedly upon the nature of the solvent. Again, we have here a clear-cut case of competition between ligand and solvent, depending upon the electron-donor ability of solvent molecules (table 8).

^7Li and ^{23}Na NMR were used to determine the formation constants of 1:1 complexes between alkali metal ions and various acyclic ligands, as indicated in table 9 (Cornélis *et al* 1982).

NMR methods have been used also to determine the stoichiometry and the thermodynamics of the interaction between cations and sugars in various solvents. In water, Angyal (1973, 1974) showed that its occurrence is highly specific of an *axial-equatorial-axial* sequence of OH groups. In low dielectric solvents such as pyridine or isopropylamine, sodium perchlorate interacts with a variety of sugars, forming 1:1 complexes (Detellier *et al* 1976). The interaction, of moderate strength, is best described as non-specific, since a variety of sugars display comparable formation constants as shown in table 10. (Grandjean and Laszlo 1977). These authors concluded that the Na^+ -sugar interaction is best described as non-specific, with close proximity of the ionic partners maintained, as in a sugar-shared ion pair.

Table 8. Stability constants of the LiClO_4 -NDA complexes.

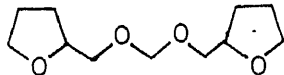
Solvent (donor number)	$K_{1/2}$	K_1	$K_2 \text{ (M}^{-1}\text{)}$
Methylene chloride (~ 0)	—	$\approx 10^6$ (?)	200 ± 25
Nitromethane (2.7)	50 ± 10	10^5 – 10^6	17 ± 3
Acetonitrile (14.1)	—	1000 ± 300	10 ± 2
Pyridine (33.1)	—	1.1 ± 0.1	—

Olsher *et al* 1980.

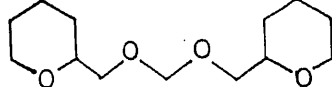
Table 9. Binding constants of Li^+ and Na^+ for LiClO_4 and for Na BPh_4 in nitromethane at 303 K.

Ligand	$\text{Li}^+ : K \text{ (M}^{-1}\text{)}$	$\text{Na}^+ : K \text{ (M}^{-1}\text{)}$
<u>1</u>	—	40 ± 5
<u>2</u>	—	50 ± 5
<u>3</u>	—	—
<u>4</u>	—	—
<u>5</u>	400 ± 40	45 ± 10
<u>6</u>	50 ± 10	6 ± 1.5
<u>7</u>	(to be determined)	(to be determined)
<u>8</u>	> 2.000	60 ± 10

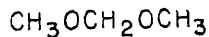
A dash indicates the absence of any significant interaction



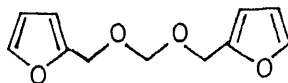
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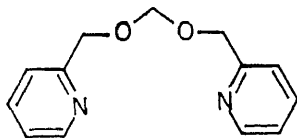
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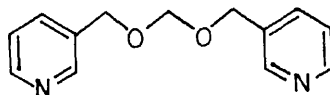
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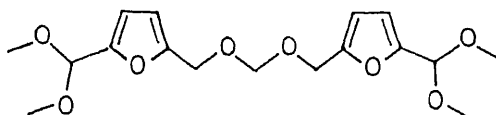
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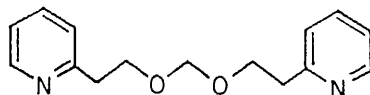
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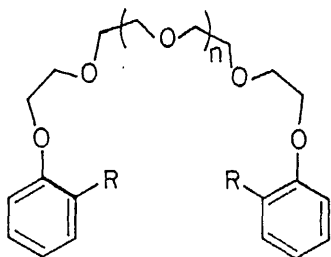


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Table 10. Characteristics of sugar-sodium cation complexes at 290 K.

Sugar/solvent	K_f (M^{-1})
Sorbose/pyridine	7.2 ± 2.2
Sorbose/isopropylamine	19.0 ± 4.0
Methyl- β -D-ribofuranoside/pyridine	5.5 ± 0.6
Methyl- β -D-ribofuranoside/isopropylamine	12.7 ± 1.4
Ribose/pyridine	6.8 ± 1.3
<i>p</i> -Methoxy-phenyl- β -D-galactopyranoside/pyridine	13.3 ± 1.8
Sorbitol/pyridine	11.2 ± 2.1
Lactose/pyridine	8.0 ± 1.6

^{23}Na linewidths $\Delta\nu_{1/2}$ have served as observables in determining the thermodynamics of complex formation between Na^+ ions and various acyclic polyethers in pyridine solution (Grandjean *et al* 1981). These ligands differ in the number of heteroatoms capable of binding the cation. After determination of the 1:1 stoichio-



- 9 $n = 1$ $R = -\text{NHCOCH}_3$ (O_5N_2)
 10 $n = 3$ $R = -\text{NHCOCH}_3$ (O_8N_2)
 11 $n = 1$ $R = -\text{CONHCH}_3$ (O_5N_2)

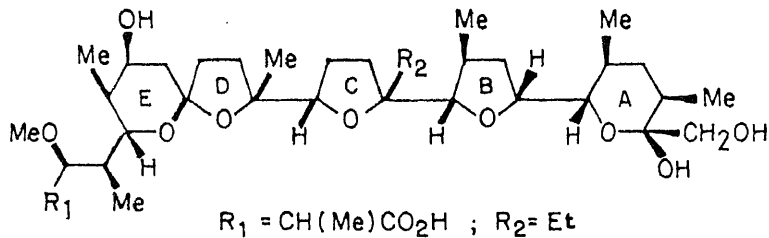
metry, the linewidth (normalized to unit viscosity) was determined as a function of the molar ratio of ligand to cation. Fast exchange conditions prevailed, so that the observed ^{23}Na linewidth was the weighted average between the free and the complexed states. Analysis of the experimental curves obtained at several temperatures gave the results shown in table 11. Two points should be noted. Firstly, the entropies of 1:1 complex formations are very strongly negative, *despite* the release by the ion of some (or all) of its solvating molecules upon complex formation. Secondly, the ΔH^0 and ΔS^0 values differ very much for the $10 \cdot \text{Na}^+$ complex, as compared to the other two complexes. The explanation relies upon similarity between the solution structures of these complexes and their solid-state structures as revealed by X-ray studies: ligands 9 and 11 wrap in helical manner around the metallic ion, but the number of heteroatoms available for coordination (a total of seven) is insufficient for full spherical encapsulation of the cation; hence, the ion continues to be solvated in the complex. One or two solvent molecules continue to coordinate to Na^+ in the complex with 9 or 11. This explains the very strongly negative ΔS values: immobilization of solvent molecules translates into loss of *translational* entropy, in addition to the *rotational* entropy loss, from the freezing-out of degrees of freedom for internal rotation, as the ligand wraps around the cation. Only this latter term is present for the $10 \cdot \text{Na}^+$ complex, since ligand 10 has enough ligating atoms (a total of 10) for full spherical wrapping of the sodium cation. In other words, ligands 9 and 11 compete with the (good donor) solvent pyridine for access to the sodium ion. Ligand 10, by contrast, is able to shield Na^+ effectively from the solvent.

Table 11. Thermodynamic parameters for the complexation of Na^+ by acyclic polyethers in pyridine solution.

Ligand	ΔH^0 (kJ mol^{-1})	ΔS^0 ($\text{JK}^{-1} \text{mol}^{-1}$)
<u>9</u> (O_5N_2)	-66 ± 10	-185 ± 45
<u>11</u> (O_5N_2)	-45 ± 7	-115 ± 25
<u>10</u> (O_8N_2)	-18 ± 3	-11 ± 3

The Na^+ complexes of 'short' ligands such as **1** or **3** are predicted to be more solvated in acetonitrile than in pyridine. Indeed, comparison of the results for **1** in pyridine (table 11) and in acetonitrile is striking: in the latter solvent the complexation entropy is close to zero and the acetonitrile molecule is too weak an electron donor to coordinate to the Na^+ cation. In other words, the lower entropy which would result from coordination of acetonitrile is insufficient to offset the attendant loss in translational entropy (Grandjean *et al* 1981).

Just as synthetic acyclic ligands are capable of wrapping themselves around a cation, there exist a number of natural polyethers which constitute an important class of the antibiotic ionophores. Borremans and Anteunis have recently published (1981) a statistical treatment to predict the ^1H NMR spectrum of seventeen polyether ionophores, mainly open chain such as monensin or nigericin. Predictions can be made for shifts of 0.19 ppm in the case of fragments in pyranoid rings, and could be very useful for the determination of the ionophore-cation complex geometry (Borremans and Anteunis 1981). This statistical treatment follows upon the gathering of a huge quantity of ^1H NMR data on such complexes obtained in the Ghent group (Anteunis, Anteunis and Rodios 1981; and references therein). A representative structure is monensin (a molecule widely used as part of the chickenfeed): The monensin



complex will serve to describe and explain the kinetic results which can be extracted from NMR data for ion-molecule complexes.

When the relaxation rate T_1^{-1} is plotted against reciprocal temperature (figure 1) for $^{23}\text{Na}^+$ in methanol, in the presence of monensin, a 'textbook case' is found (Borremans 1977): there is a nice sigmoidal change of the relaxation rate. The transition corresponds to chemical exchange at moderate rate ($1/T'_{1A}$), the straight line behaviour at low temperatures approximates asymptotically the experimental results for free Na^+ ions (state A) under the same conditions ($1/T_{1A}$). Combining the information from T_{1A}^{-1} and the $(T'_{1A})^{-1}$ curves yields the calculated T_{1B}^{-1} line for bound Na^+ ions (state B) in the Na^+ -monensin complex. The equilibrium condition is $P_A/\tau_A = P_B/\tau_B$, where P_A and P_B are mole fractions, τ_A and τ_B residence times. The exchange rate $k_a = 1/\tau_a$ is calculated from the measured parameters T'_{1A} , T_{1A} and T_{1B} , according to the equation

$$\frac{1}{\tau_A} = \frac{(1/T_{1B} - 1/T'_{1A})(1/T'_{1A} - 1/T_{1A})P_B}{P_A/T_{1A} + P_B/T_{1B} - 1/T'_{1A}}$$

† Even if it is not true, is it well conceived?

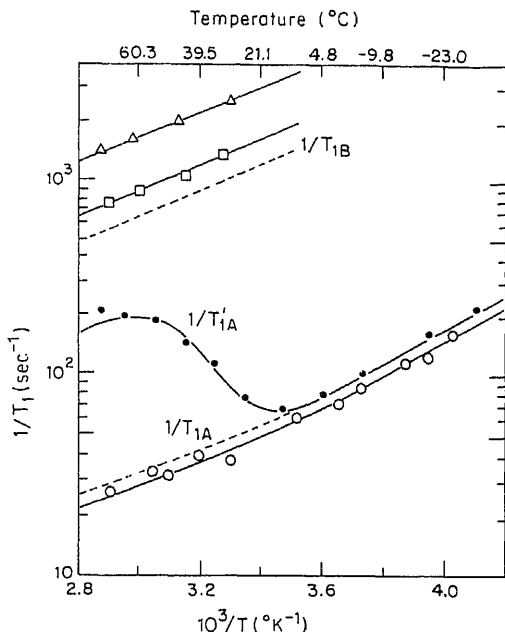


Figure 8. Semilog plot of the longitudinal relaxation rate for ^{23}Na in methanol vs reciprocal temperature; solution composition: 0.5 M NaBr ($\circ$); 0.15 M monensin- Na^+ and 0.35 M NaBr ($\bullet$); 0.3 M monensin Na^+ ($\square$) and 0.65 M monensin Na^+ ($\triangle$) (from Degani 1977).

The exchange rates, when measured at 35°C for different monensin (sodium salt MonNa) concentrations (0.125–0.3 M) and with a constant concentration ratio $[\text{MonNa}]/[\text{Na}^+] = 3/7$, were found to be invariant. This finding points to a first-order dissociative mechanism:



These rate constants, together with the corresponding Eyring activation enthalpies and entropies, are compared in table 12 with data pertaining to valinomycin, a cyclic antibiotic ionophore, and to dicyclohexyl-18-crown-6 (DCC).

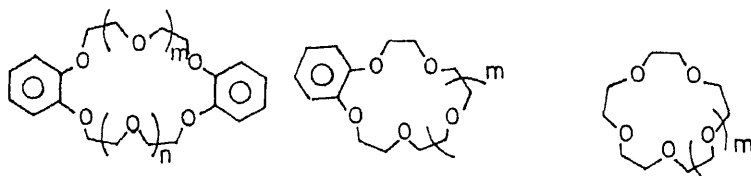
To end this section, one word about the controversial topic of the interaction between metal ions and nucleotides: for reviews, see Tu and Heller (1974); Frey and Stuehr (1974); Marzili (1977); Hodgson (1977); Pezzano and Podo (1980). We discuss

Table 12. Formation and dissociation rate data for the complexations with sodium ions in methanol at 25°C.

elsewhere (§4.1) the question of the identification of the binding sites which, together with the stoichiometry of the complexes present, has been most debated.

3.2 Monocyclic ligands

In the cases just evoked, *viz* in the complexation of a cation by an open chain ligand, such as glymes, polyamines or some antibiotics, the ligand coils round the cation (the so-called chelate effect). The cavity in which the cation is nested is formed during the process of complexation. One can use cyclic ligands with preformed cavities, either monocyclic ('crown' compounds), bicyclic ('cryptands') or polycyclic. We shall first consider the case of the monocyclic ligands, and mainly of cyclic ligands with oxygen as the main donor atom (Pedersen 1967). For this case, we will refer to crown compounds by using the usual nomenclature: for example, DB18C6 for dibenzo-18-crown-6 (6,7,9,10,17,18,20,21-octahydro-dibenzo[b,k] [1,4,7,10,13,16]hexaoxacyclooctadecan). We will travel through the abundant literature on this topic with regard to stoichiometrics, thermodynamics, geometry, kinetics and microdynamics of the interactions.



DB12C4: $m = n = 0$

DB15C5: $m = 1; n = 0$

DB18C6: $m = n = 1$

DB21C7: $m = 2; n = 1$

DB24C8: $m = n = 2$

DB27C9: $m = 3; n = 2$

DB30C10: $m = 3; n = 3$

MB-3x-C-x; $m = x-4$ 3x-C-x, with $m = x-4$

A simplified general case of the complexation of a cation by a crown is depicted below:



$(M^+, C)_s$, $(C, M^+, C)_s$, $(M^+, C, M^+)_s$ are the complexes of stoichiometries 1:1, 2:1, 1:2. Stoichiometries of this kind have been shown to occur in the solid state: for example K^+ can form 1:1 complexes with DB30C10 (Hasek *et al* 1980; Busch and Truter 1972), or 2:1 complexes with DB24C8 (Mercer and Truter 1973) when Li^+ and 12C4 form 1:1 (Groth 1981) or 1:2 complexes (Dale and Krane 1972).

In solution, depending on the nature of cation, of solvent, of crown, or of temperature, the three equilibrium constants, K_{f1} , K_{f2} , K_{f3} will be very different. In the case of a cation like K^+ , complexed by a small crown, such as 15C5, one can predict a very small value of K_{f3} , and a significant value of K_{f2} , depending on the solvent. If the solvent is a poor donor, like acetonitrile ($D_N = 14.1$) or nitromethane ($D_N = 2.7$),

predict, on this very simple basis, that in the case of Li^+ , complexed by 12C4, in DMSO $K_{f1} \gg K_{f2} \gg K_{f3}$, and K_{f1} should be the only measurable constant. On the contrary, in the case of Na^+ , complexed by 30C10 in nitromethane, K_{f3} should be high enough to permit the formation of the 1 : 2 (crown : cation) complex; and in a better donor solvent, such as DMSO, K_{f1} should be the only measurable equilibrium constant: $K_{f1} \gg K_{f2}$, K_{f3} .

One can simulate the chemical shift of the alkali cation to be expected by varying the [crown]/[cation] ratio in a given solvent, taking into consideration the three equilibria above. The system of six equations binding the unknowns ($[\text{M}^+]$, $[\text{C}]$, $[\text{C}, \text{M}^+, \text{C}]$; $[\text{M}^+, \text{C}, \text{M}^+]$, $[\text{M}^+]$, $[\text{C}]$, δ_{obs}) to the variables (K_{f1} , K_{f2} , K_{f3} , $[\text{M}^+]_0$, $[\text{C}]_0$, δ_0 , δ_{I} , δ_{II} , δ_{III}) can be easily reduced to a system of two equations of the third degree in $[\text{M}^+]$ and $[\text{C}]$.

δ_{obs} , δ_0 , δ_{I} , δ_{II} and δ_{III} are respectively the observed chemical shifts and the characteristic chemical shifts of M^+ , (M^+, C) ; $(\text{C}, \text{M}^+, \text{C})$ and $(\text{M}^+, \text{C}, \text{M}^+)$.

$$[\text{M}]_0 = [\text{M}^+] + K_{f1} [\text{M}^+] [\text{C}] + K_{f1} K_{f2} [\text{M}^+] [\text{C}]^2 + 2 K_{f1} K_{f3} [\text{M}^+]^2 [\text{C}] \quad (28)$$

$$[\text{C}]_0 = [\text{C}] + K_{f1} [\text{M}^+] [\text{C}] + 2 K_{f1} K_{f2} [\text{M}^+] [\text{C}]^2 + K_{f1} K_{f3} [\text{M}^+]^2 [\text{C}]. \quad (29)$$

This system is solved by the Newton-Raphson method. $[\text{M}^+]$ and $[\text{C}]$ being calculated, δ_{obs} is given by:

$$\delta_{\text{obs}} = \frac{[\text{M}^+]}{[\text{M}^+]_0} \delta_0 + \frac{K_{f1} [\text{M}^+] [\text{C}]}{[\text{M}^+]_0} \delta_{\text{I}} + \frac{K_{f1} K_{f2} [\text{M}^+] [\text{C}]^2}{[\text{M}^+]_0} \delta_{\text{II}} + \frac{2 K_{f1} K_{f3} [\text{M}^+]^2 [\text{C}]}{[\text{M}^+]_0} \delta_{\text{III}} \quad (30)$$

The simulated graphs are given in figure 9. They all have been obtained with $[\text{M}^+] = 0.02 \text{ M}$, a value usually found in the literature. At this concentration, ion pairing is usually negligible (Detellier and Gerstmans 1982).

A simulation for typical values of ^{23}Na NMR is given in figure 9 with $\delta_0 = 15 \text{ ppm}$ (close to the value for NaClO_4 0.02 M dissolved in nitromethane), δ_{I} (M^+C), δ_{II} ($\text{C}, \text{M}^+\text{C}$), δ_{III} ($\text{M}^+, \text{C}, \text{M}^+$) have received arbitrarily the values 20, 10, 1 and K_{f1} the value 3000. In figure 9a K_{f2} and K_{f3} are varied.

The typical case of the formation of a complex 1 : 1, not perturbed by complexes with other stoichiometries is obtained when $K_{f2} = K_{f3} = 0.1$. The graph consists of two straight lines with an intersection at a ratio $[\text{C}]/[\text{Na}^+] \simeq 1.0$.

Under the same conditions for a value of K_{f3} as low as 10, a sigmoidal curve is obtained which could permit, if such a case is encountered in an experiment, the calculation of the two equilibrium constants. When K_{f3} and K_{f1} become commensurate, in the conditions of limiting chemical shifts which are chosen, a sharp well is found with a minimum at the stoichiometric ratio 2 : 1 and an inflexion point around

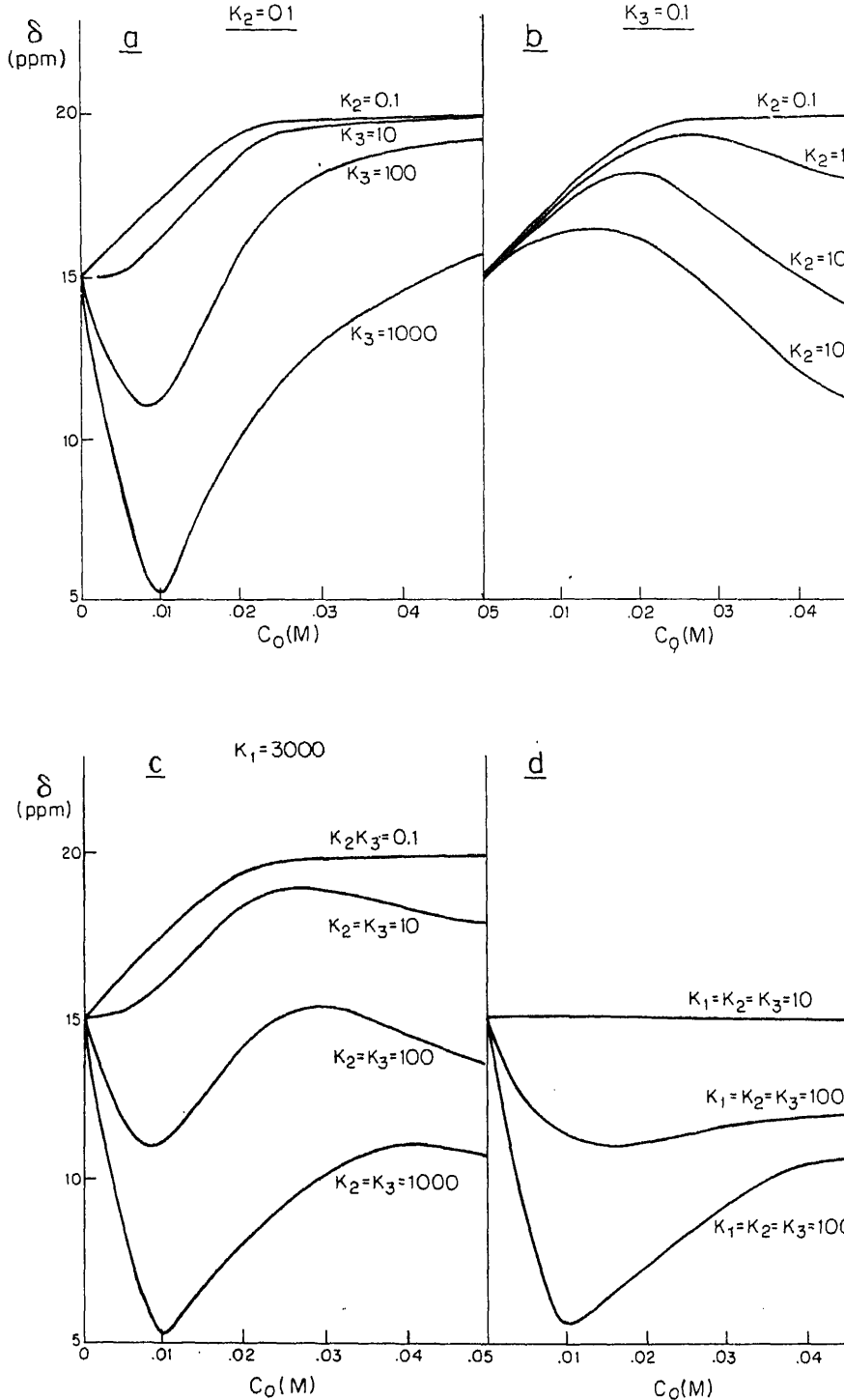


Figure 9. Simulation of the ^{23}Na chemical shift variation for the case of

handsome curves is hard to resist. We shall pass now to a rapid description of what has indeed been found experimentally.

Popov and his coworkers have covered this area by studies in alkali-ion NMR, mainly ^7Li , ^{23}Na and ^{133}Cs , of the interaction between those cations and the smallest crown 12C4, to the large DB30C10. The plot of the chemical shift, or of the linewidth at half height gives a very rapid answer to the question of the stoichiometry. Thus, 1:1 and 2:1 (sandwich) complexes are observed between the lithium ion and 12C4 in nitromethane or propylene carbonate solutions while, surprisingly, only a 1:1 complex was detected in acetonitrile solution (Smethana and Popov 1980). Also, 2:1 complexes were observed with the 18C6- Cs^+ system in a number of nonaqueous solvents (Mei *et al* 1977a, d). If the crown had a cavity large enough to accommodate the lithium cation, only the 1:1 complex has been shown to exist (figure 10). This is the case for the complexation of Li^+ by 15C5 in seven different solvents (Smethana and Popov 1980). In the case of the large crown ether, dibenzo-30-crown-10, one observes, in solvents of low donor number (nitromethane, acetonitrile), formation of the 1:2 and 1:1 complexes (Shamsipur and Popov 1979) which have been previously isolated in the crystalline form (Parsons *et al* 1975). In those solvents, the presence of two inflexion points shows unambiguously the coexistence of those two complexes with a third species which is proposed by the authors to be the 2:3 (ligand:metal) complex, but which could be also the 2:1 (figure 9) or the 1:1 complex in a different conformation. These hypotheses should be tested by a multiple parameter non-linear regression. The case of the complexation of Cs^+ by DB30C10 is more simple: only the 1:1 complex is observed. The value of the limiting chemical shift for the complex, almost constant for

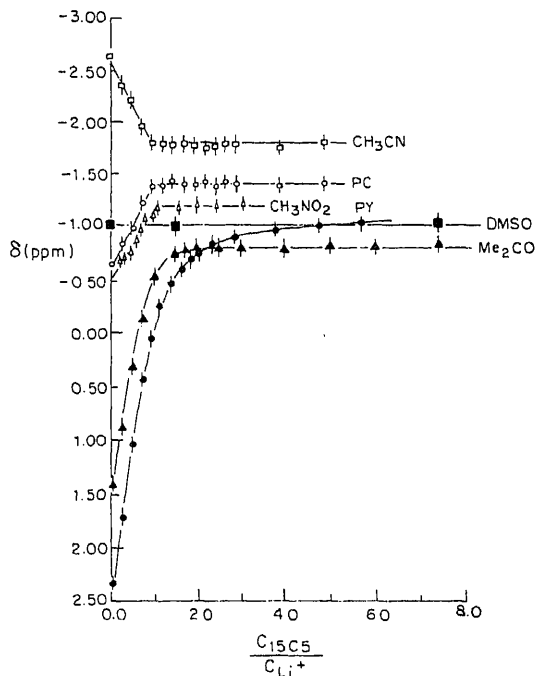


Figure 10. ^7Li chemical shifts against 15C5/ Li^+ mole ratio in various solvents [LiClO_4]

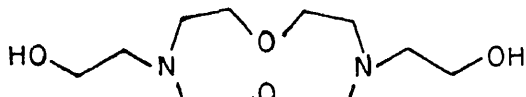
five different solvents, suggests the folding of the large crown around the cesium ion (Shamsipur and Popov 1979).

Formation of the 1 : 1 complex and the expulsion of solvents and the anion from the coordination sphere of the cation was also demonstrated in the case of dibenzo-24-crown-8 with sodium (Shamsipur *et al* 1980; Bisnaire *et al* 1982). It is to be noted that Cs^+ and DB24C8 or DB21C7 form 1 : 1 complex only and the chemical shift of the complex is very solvent-dependent, suggesting the presence of at least one solvent molecule in the solvation sphere of the cesium (Shamsipur *et al* 1980).

If the alkali-cation NMR can give very valuable information on the stoichiometries, thermodynamics, microdynamics or kinetics of the complex formation, detailed structural information is better derived from ^{13}C or ^1H NMR of the ligand. However, knowledge of the quadrupolar coupling constant of the complexed cation could provide answers to the question of the symmetry of the cation close environment. This has been rarely obtained in the case of crown ethers (Bisnaire *et al* 1982). Using ^1H and ^{13}C NMR, Live and Chan (1976) have elucidated the structure in solution of the complexes formed between monobenzo-18-crown-6, dibenzo-18-crown-6 and dibenzo-30-crown-10 and Na^+ , K^+ , Cs^+ or Ba^{2+} , in a number of solvents, with different counterions. A very interesting conclusion from their work is the fact that, if the DB30C10 wraps around the sodium as well as around the potassium cation, the geometry of the two complexes is quite different. The potassium cation is completely surrounded by the crown ether. The three-dimensional cavity formed by the folded crown ether has the right dimension to imprison the cation. This is no longer the case for the sodium, which is much less tightly bound in the cavity and can be exchanged between two or more different sites of complexation into the folded crown. One has to remember the plots obtained for the ^{23}Na chemical shift in this case (Shamsipur and Popov 1979) showing the presence of at least three different species in the whole range of $[\text{DB30C10}]/[\text{Na}^+]$ ratios. Joint relaxation studies in ^{23}Na and ^{13}C on this system should be very informative. ^{13}C relaxation times showed the rigidity of the KSCN-DB30C10 complex on the time scale of the reorientational correlation time (Live and Chan 1976). A similar conclusion was obtained for the KSCN-DB18C6 (Fedarko 1973) and the NaClO_4 -DB24C8 (Bisnaire *et al* 1982) complexes.

Levy *et al* (1980) have shown the usefulness of the ^{89}Y nucleus to study the interactions of metal ion with organic ligands. This spin 1/2 nucleus gives rise to a large $^{89}\text{Y}\{^1\text{H}\}$ NOE effect which can be used to probe the binding of the Y^{3+} cation to organic molecules. 12C4, 15C5 and 18C6 have been used to study the fixation of Y^{3+} . The complex 12C4- Y^{3+} shows a purely dipolar relaxation; spin-rotation, paramagnetic or chemical shift anisotropy contributions can be neglected. This is no longer the case when 15C5 and 18C6 are considered. Other relaxation mechanisms, particularly spin-rotation, become noticeable, which is expected if Yttrium were largely uncomplexed.

Fixation of Ca^{++} on ligand 12 was followed by ^{43}Ca NMR (Drakenberg 1982) in water solutions, at pH 10. Exchange between free and complexed calcium is very slow, two different resonances being always observed, not only for ligand I, but also for EGTA



[ethylene glycol-bis (β -ethylamine)-N,N'-tetra acetic acid] or EDTA (ethylene diamine tetraacetic acid).

Correlation times which have been calculated from the ^{13}C T_1 's permit the determination of the quadrupolar coupling constant χ for ^{43}Ca in the different complexes ($\chi = 1.4$ MHz for I). It is interesting to note that χ is much lower (0.5 MHz) in the case of EDTA showing apparently a higher symmetry of the close environment of Ca^{++} in this complex.

The relaxation of ^{133}Cs for CsI or CsCl dissolved in dimethylformamide (DMF) can be ascribed entirely to the quadrupolar relaxation mechanism (Wehrli 1977). The ^{133}Cs spin-lattice relaxation rates of the complex $\text{Cs}^+ \cdot 18\text{C6}$ surprisingly show a linear increase with a break point at $[\text{18C6}]/[\text{Cs}^+] = 2$. This indicates the formation of a 2:1 complex, but gives no evidence for the formation of a 1:1 complex which has been shown to be a ponderable species by potentiometric results (Frendsdorff 1971) or by the variation of the ^{133}Cs chemical shifts. The characteristic relaxation rate of the 1:1 complex is probably, quite fortuitously, intermediate between the relaxation rates of the 2:1 complex and the solvated cation.

More complex situations are encountered when the conjugated anion remains close to the crown complexed cation. Thus, the coexistence of monomeric and dimeric ion pairs, both of which interact with the crown ethers 15C5 or 18C6, have been reported to occur in solutions in tetrahydrofuran of the sodium salt of ethyl acetoacetate (Cornélis *et al* 1978).

The successful model used is presented in (31).



Where E is used for ethylacetoacetate, and C for Crown.

An excellent correlation between the concentration of ENaC and the rate of alkylation by $\text{C}_2\text{H}_5\text{I}$ was found, which suggests that the crowned monomeric ion pair is the single kinetically active anionic species (Cornélis *et al* 1978).

Only a small amount of work has been done to determine the kinetic parameters of the interaction crown-cation by NMR, mainly by the group from the Weizmann Institute at Rehovot (Shchori *et al* 1971, 1973; Shporer and Luz 1975). We have seen in the previous section the behavior of the ^{23}Na relaxation times when sodium ions are complexed by the ionophore monensin (Degani 1977). The same pattern is obtained when NaSCN is complexed by DB18C6 in dimethylformamide (Shchori *et al* 1971).

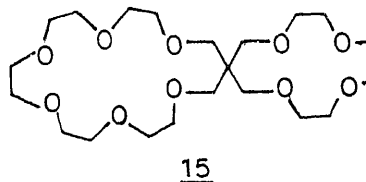
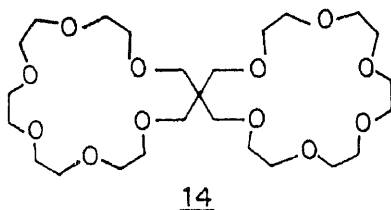
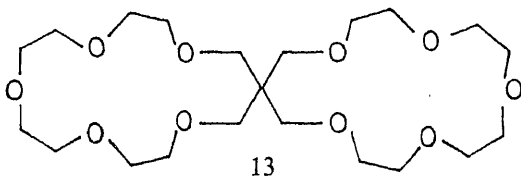
At low temperatures, there are two resonances: one, characteristic of the complexed cation, has a very large width at half height, and the other one, characteristic of the solvated cation, is observed. Increasing temperature induces a broadening of the resonance line until a maximum is reached, at the limit of fast exchange. At higher temperatures, only one resonance is observed, averaging the two environments of the sodium cation. Equation (23) is applicable and the attendant kinetic parameters can be derived. Complexation of sodium with dicyclohexyl-18-crown-6 (DC18C6) in meth-

same formalism (Shporer and Luz 1975). The exchange rate for rubidium was too slow to be followed by this technique.

Very interestingly, an activation energy of 12 kcal coincides with the activation energy required in a ring system for four trans to gauche conformational changes (M R Truter, private communication cited by Shchori *et al* 1973). Thus, conformational changes of the ligand around the sodium cation during the process of decomplexation are very likely to be the rate-determining factors. Lower energy barriers are found in the case of DC18C6 (8.3 kcal/mol) which is more flexible than DB18C6, and an energy barrier of 12.6 kcal/mol was found in the case of decomplexation of potassium by DB18C6 (Shporer and Luz 1975).

Decomplexation kinetic parameters for the Cs^+ -DC18C6 complex in propylene carbonate and for the Cs^+ -18C6 complex in pyridine (Mei *et al* 1977d) have been obtained with $\Delta G^\ddagger$ (25°C) value of 12 kcal/mol, a $\Delta H^\ddagger$ of +8 kcal/mol and a $\Delta S^\ddagger$ of -14 e.u. This negative entropy value contrasts with positive values in the case of cryptands, to be discussed in the next section.

Even though spiro-bis-crown ethers (13-15) could be considered as bicyclic ligands, we will consider the study in this section. One or two metallic ions are able to at



themselves to such spiro bicycles ('dicoronands'). Complexation of NaClO_4 by the crown ethers in pyridine solutions was followed by ^{23}Na NMR (Bouquant *et al* 1977). Dicationic 1:2 complexes were shown to be formed, in equilibrium with

Table 13. Formation constants for the 1:1 complex (subscript 1) and for the 1:2 complex (subscript 2) of Na^+ and 13.

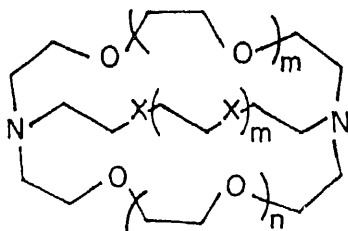
T (K)	K_1 (M^{-1})	K_2 (M^{-1})
278.2	800	26
293.2	750	18
307.2	550	31
323.2	475	24.5
338.2	380	40
353.2	350	25.5

$\Delta H^\circ = -2.3 \pm 0.2 \text{ kcal mol}^{-1}$; $\Delta S^\circ = +5.1 \pm 0.8 \text{ e.u.}$ for the formation of the complex 1:1.

3.3 Bicyclic and polycyclic ligands

Macrocyclic ligands form cryptate-type cation inclusion complexes which are more stable than those formed with monocyclic ligands (crown-type). Moreover, the cation exchange between the bulk of the solution and the cage formed by the ligand is slower (Lehn 1973). When included into such a cavity, the cation coordination shell is well defined, and protected from direct contact with solvent molecules (see §2.5b).

By a study in ^{23}Na and ^{13}C NMR ('the double nuclear spin probe method'), Kintzinger and Lehn (1974) were able to obtain the reorientational correlation time and the quadrupolar coupling constant (see (17)) for the sodium cation complexed by four macrobicycles depicted below:



16 $m = 0; n = 1; X = \text{O}$ (C211)

17 $m = 1; n = 0; X = \text{O}$ (C221)

18 $m = n = 1; X = \text{O}$ (C222)

19 $m = n = 1; X = \text{S}$.

The ^{23}Na quadrupolar coupling constants decrease when the number of oxygens in the ligand shell increases, showing a higher symmetry for the cation environment. Moreover, the chemical shift is linearly related to the quadrupolar coupling constant, what is theoretically expected if the paramagnetic shielding term dominates the ^{23}Na chemical shifts (Deverell 1969). This trend has been confirmed in the case of the monocyclic DB24C8- Na^+ cation (Bisnaire *et al* 1982). The ligand adopts a folded conformation and isolates the cation from the solution, in a cryptate-like

between Na^+ and the indicated ligand.

Ligand	δ^a (ppm)	χ_{Na} (MHz)
<u>16</u> ^b	+11.15	2.20
<u>17</u> ^b	-4.25	1.43
<u>18</u> ^b	-11.40	1.01
<u>19</u> ^b	-6.20	1.38
DB24C8 ^c	-9 to -7	0.8-1.2

^a δ is measured with respect to a 0.25 M NaCl solution in water;

^b Kintzinger and Lehn 1974; ^c Bisnaire *et al* 1982; the range of values is given for the solvents: CDCl_3 , pyridine, acetonitrile, nitromethane, acetone, methanol and propylene carbonate.

When excess NaCl is added to the cryptate solutions in methanol, two separate signals are observed at 35°C, giving a $\Delta G^\ddagger$ of about 15.4 kcal/mol (331 K) for complex [18, Na^+], and a $\Delta G^\ddagger > 16$ kcal/mol (331 K) for [16, Na^+] and [17, Na^+], which is very close of the value previously found by Ceraso and Dye (1973) for complex [18, Na^+] in ethylene diamine ($\Delta G^\ddagger = 14.8$ kcal/mol at 323 K).

The exchange kinetics of the sodium cation with 2,2,2-cryptate complexes has been studied in water, ethylenediamine, tetrahydrofuran and pyridine (Ceraso *et al* 1977). A detailed analysis of the curves (figure 11) furnished the activation parameters for exchange (table 15).

As one can see the activation entropies of decomplexation are negative for (C222) (Ceraso *et al* 1977) and for (Li^+ , C211) or (Li^+ , C221) (Cahen *et al* 1975) in aqueous solvents, and positive in water. The well-structured bulk water around the hydrophobic complex formed by the cation and the cryptate is disturbed by the incoming of the cation into the solution. In non-aqueous solutions the negative $\Delta S^\ddagger$ reflects the participation of the solvent in the transition state. The values of $\Delta S^\ddagger$ between -8 and -23 e.u., correspond very roughly to the loss of translational entropy of one solvent molecule. When the diameter of the cation is greater than the cavity

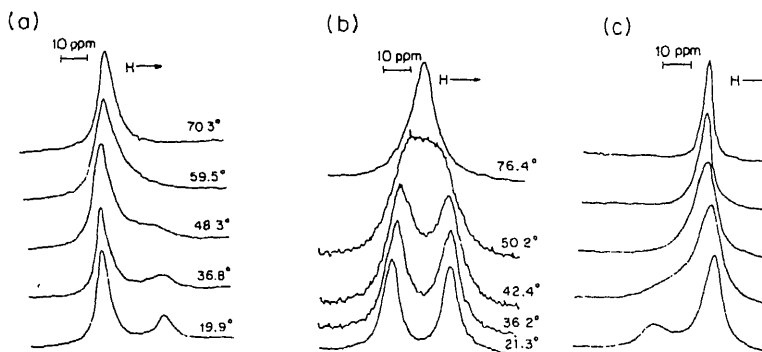


Figure 11. ^{23}Na spectra at various temperatures for solutions of Na^+ with C222 and ethylenediamine (EDA), (a) 0.15 M C222 and 0.6 M NaBr, (b) 0.30 M C222 and 0.6 M NaBr, (c) 0.45 M C222 and 0.6 M NaBr.

Table 15. Decomplexation activation parameters.

Complex	Solvent	$\Delta H^\ddagger$ (kcal mol ⁻¹)	$\Delta S^\ddagger$ (e.u.)
(Na ⁺ , C222) ^a	Py	13.6	-12.6
	THF	13.8	-8.1
	H ₂ O	16.1	+5.3
	EDA	12.3	-7.6
(Li ⁺ , C211) ^b	Py	19.0	-12.5
	H ₂ O	20.7	+0.4
	DMSO	15.5	-13.8
	DMF	15.4	-15.5
(Li ⁺ , C221) ^b	F	13.5	-22.8
	Py	12.9	-14.9

Decomplexation activation parameter for (Na⁺, C222), (Li⁺, C211) and (Li⁺, C221) in pyridine (Py), tetrahydrofuran (THF), water, ethylenediamine (EDA), dimethylsulphoxide (DMSO), dimethylformamide (DMF) and formamide (F), ^aCeraso *et al* 1977; ^bCahen *et al* 1975.

of the cryptand, one expects to observe the formation of complexes where the cation is not located in the center of the cavity and contains some residual solvent molecules into its coordination shell. This was observed by ¹³³Cs NMR for the case of the Cs⁺ complexation by the cryptand C222 (Mei *et al* 1977c). Two types of 1:1 complexes were shown to coexist in solution: inclusive and exclusive.



The activation parameters were obtained only for solutions in DMF, where process 1 (formation of the exclusive complex) is the dominating mechanism: $\Delta H^\ddagger = 12.9 \text{ kcal} \cdot \text{mol}^{-1}$ and $\Delta S^\ddagger = +17 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{deg}^{-1}$. The value of $\Delta S^\ddagger$ is in strong contrast with the activation entropies of decomplexation of the cryptates shown in table 14 or with the value found for the complex Cs⁺-18C6 ($\Delta S^\ddagger = -14 \text{ e.u.}$). This large positive entropy variation is difficult to interpret: participation of solvent in the transition state should lead to negative values and configurational entropy changes should not contribute to such a high value. C211 and C221 form the exclusive complex with Cs⁺ only (Mei *et al* 1977b).

Kinetic stability of the specific complexes [Li⁺, C211] and [K⁺, C222] has permitted to determine unambiguously the ⁷Li NMR signal of the triple ion formed between Li⁺ and the acetoacetate enolate anion (E-Li-E)⁻ (M⁺, C) (Cambillau and Ourevitch 1981). The ⁷Li chemical shift of (E-Li-E)⁻ is affected by the nature of the solvent (CH₂Cl₂ (-2.1 ppm) or DMSO (-1.7 ppm)).

Cryptand (2,2,2) cleaves the iodine molecule to form the inclusive complex (I⁺, C222) I⁻ (Pierre *et al* 1980). Positive halogen ion cryptation sends us back to the other side of the periodic table: cryptands permit the formation of the alkali metal anions. A crystalline salt of the sodium anion (Na⁻) has been shown to be formed in ethylamine solutions of the cryptand 2,2,2. The stoichiometry is (Na⁺, C222) Na⁻ (Dye *et al* 1974). The ²³Na NMR of these species is shown in figure 12. Two signals are observed

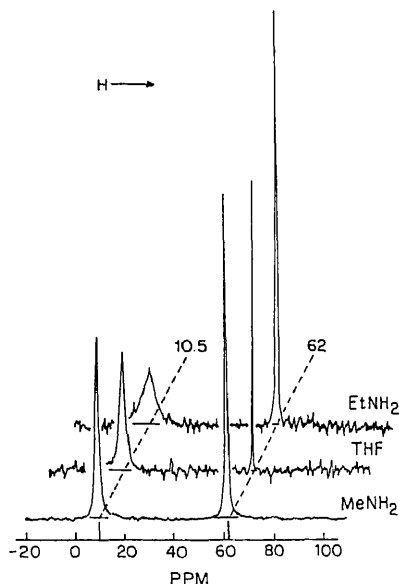
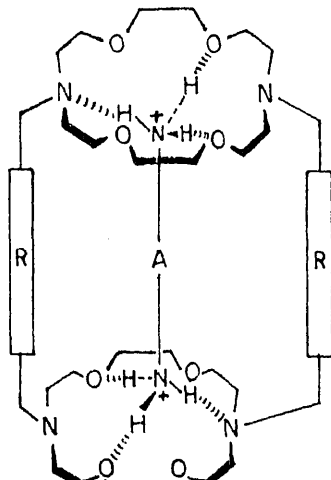


Figure 12. ^{23}Na spectra of $\text{Na}^+ \text{-C222- Na}^-$ solutions ($\approx 0.1 \text{ M}$) in three solvents (Dye *et al* 1977).

linewidth of Na^- in THF is less than 3 Hz compared with 23 Hz for Na^+ in THF. The extreme narrowness of the line for Na^- attests to the high spherical symmetry of the species (Dye *et al* 1975). Rb^- and Cs^- have also been observed by ^{87}Rb and ^{133}Cs NMR. As for Na^- , these anions give narrow lines which are diamagnetically shifted (Dye *et al* 1975).

Macrobicyclic molecules forming cation inclusion complexes have been synthesized (Graf and Lehn 1975). They form complexes of stoichiometries 2:1 (metal:cryptand) in the case of Ag^+ and Ba^{++} as was shown by ^1H and ^{13}C NMR (Lehn and Simon 1975). Diammonium molecules fit into the cavity of macrotricyclic receptors (20).



Kintzinger *et al* (1981) have shown by ^{13}C nuclear relaxation times measurements that the structural complementarity between the receptor molecular and the substrate molecule is reflected in a strong dynamic coupling. The complex is stable not only thermodynamically or kinetically, but also exhibits dynamic cohesion: the molecular motions of the two entities of which it is composed are coupled.

4. Interaction between ions and biomolecules

The importance of the topic now to be discussed would deserve a full volume being devoted to it! In the limited format of this review paper, we can do no more than emphasize a few salient points. The reader should also be reminded of the forewarning we gave in the introduction: this account is oriented very much towards interpretation of the results from the NMR of the quadrupolar ions themselves; and the choice of the examples to be presented is dictated to a large extent by our own familiarity with these systems, because we have ourselves worked on their elucidation.

4.1 Identification of the binding sites

Biomolecules could be portrayed, in the general sense, as molecules with molecular weights at least 500 and very often 5000 or (much) more. Hence, the first question is to ascertain where, *i.e.* to which part of this large molecule a given ion will attach itself. The NMR spectrum of the ion is not very informative in this respect, except in the all-too-rare cases in which scalar couplings between the ionic nucleus and the nuclei on the biomolecule can be detected. Even if the chemical shift of the ionic nucleus is perturbed upon binding to the biomolecular host, it will rarely be possible to infer from this *single* observable the exact location (coordinates) of the ion with respect to the biomolecule.

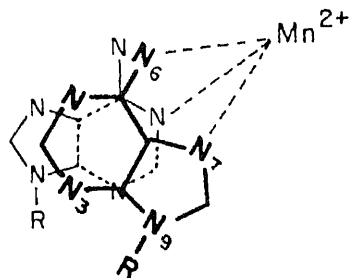
Since more than one observable is needed, one usually looks for changes in the chemical shifts and/or linewidths of *several* nuclei of the biomolecule, which will indicate qualitatively, and perhaps semi-quantitatively, the approximate site of binding. A set of techniques very generally resorted to, following the pioneering work of the Oxford group of Prof. R J P Williams, is *isomorphous replacement* of a biologically-relevant ion (such as Ca^{++}) by a paramagnetic ion, often a lanthanide ion, having a comparable ionic radius (Eu^{3+} , for instance). From the magnitudes of the induced paramagnetic shifts, one can then infer approximate distances between the ionic nucleus and neighbouring host nuclei, in the complex.

Such an approach has been applied also to complexes between paramagnetic metal ions and nucleotides, by investigation of the effect of the paramagnetic probes upon ^{31}P relaxation times (Mildvan and Cohn 1970; Brown *et al* 1973; Mildvan 1977, 1979).

A difficult question is that of the site of binding of Mg^{++} ions to adenosine triphosphate (ATP). Magnesium (II) ions are diamagnetic, and they do not form with ATP substitution-inert complexes which are sufficiently long-lived for x-ray structural determinations to be of assistance. Indeed this question has been somewhat controversial: while some authors have interpreted ^{31}P chemical shift changes as implying that Mg^{2+} interacts with both the α - and γ -phosphate of ATP (Cohn and Hughes 1962), others have used essentially the same data as evidence for interaction only with the β -phosphate group (Tran-Dinh *et al* 1975), or as implying that the Mg^{2+} -ATP complex is an $\alpha\gamma$ -tridentate (Kuntz and Swift 1973). The disparity of interpretations could not be

methods have been explored. Rather recently, for instance, a new attempt at structural characterization of the Mg^{2+} -ATP complex was made, using ^{17}O NMR. From the observed line broadenings R (corrected for various factors) of the ^{17}O resonances (table 16), it would appear that Mg^{2+} interacts approximately equally with the β - and the γ -phosphate group of ATP, and to a somewhat lesser extent with the α -phosphate of ATP (Huang and Tsai 1982).

Another type of NMR technique, the recourse to paramagnetic relaxation of spin $1/2$ nuclei, has been applied to the interaction between Mn^{2+} and adenosine monophosphate (AMP) (Levy and Dechter 1980). These authors have measured ^{15}N and ^{13}C electron-nuclear relaxation times (T_1^e) for the nuclei in the adenine, and ^{31}P T_1^e 's for the phosphate group of AMP. Under the conditions of their experiments, *viz* the high concentrations of AMP demanded by natural abundance ^{15}N NMR (0.8 M!), the nucleotides form stacked complexes. Their results are summarized in table 17. The r^{-6} dependence of the dipolar T_1^e values allowed them to determine the distances of the Mn^{2+} ion indicated in the table: it is apparent that N(1), $\text{NH}_2(6)$ and N(7), together with the phosphate *via* one of its oxygens, must all be directly bound to the paramagnetic ion. By contrast, N(3), N(9) and C(4) must all be remote from the Mn^{2+} center. Hence, the local structure about the Mn^{2+} is best represented as the following 1:2 metal-nucleotide complex (Levy and Dechter 1980):



4.2 Enhanced quadrupolar relaxation of the bound ion

Historically, Prof. Baldeschwieler seems to have pioneered the use of the considerable line broadenings undergone by a quadrupolar ion upon binding to a biomolecule (Stengle and Baldeschwieler 1966, 1967; Haugland *et al* 1967). To quote from what one of us described of this method in a textbook (Laszlo and Stang 1971): 'Rather sharp lines ($\Delta\nu_{1/2} \approx 10$ Hz) are seen for the ^{35}Cl resonance of the spherically solvated chloride ion Cl^- when sodium chloride is dissolved in water. Since the field gradient q at the quadrupolar chlorine nucleus is zero, the e^2qQ term is also zero, and quadrupolar relaxation is powerless to broaden the magnetic resonance of the ^{35}Cl . However, when this ^{35}Cl nucleus is engaged in covalent bonding, the quadrupolar coupling constants e^2qQ are then observed to be in the range of 40–90 MHz. The bandwidths are comparably large: for carbon tetrachloride $\Delta\nu_{1/2} = 14.5$ kHz, corresponding to a correlation time $\tau_c \approx 1.7 \times 10^{-12}$ sec. The idea behind the experiments to be presented now is thus very simple: the range of values between ≈ 10 and 14,500 Hz is enormous, and can be exploited if fast exchange between two such sites

Table 16. Normalized line broadenings R , at several spectrometer frequencies, for the α -, β -, and γ -phosphate groups of ATP (Huang and Tsai 1982).

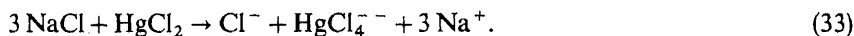
[ATP] (mM)	Position obsd.	ν_0 (MHz)	^{17}O line broadening R^a
25	α	40.67	1.1
45	α	33.9	0.9
25	α	27.11	0.7
100	α	24.4	0.9
100	α	12.2	0.8
25	β	40.67	1.4
45	β	33.9	1.7
25	β	27.11	1.7
25	β	48.8	1.4
25	β	10.85	1.4
25	γ	40.67	2.5
45	γ	33.9	1.8
25	γ	27.11	2.1
25	γ	10.85	1.8

$$^a R = (\Delta\nu_{1/2}^B - \Delta\nu_{1/2}^F) / (\Delta\nu_{1/2}^F).$$

Table 17. Diamagnetic T_1 s, dipolar T_1^e s and calculated distances for Mn^{2+} -AMP stacked complex (Levy and Dechter 1980).

Nucleus	T_1^{dia} (sec)	$T_1^e(\text{C}) \times 10^4$ (sec)	r (Å)
N(1)	4.4	0.30	2.1
C(2)	0.25	5.8	4.8
N(3)	2.8		> 5
C(4)	3.0	28	6.2
C(5)	5.3	4.9	4.6
C(6)	2.1	7.3	4.9
$\text{NH}_2(6)$	1.4	0.26	2.1
N(7)	3.2	0.20	2.0
C(8)	0.25	1.9	3.9
N(9)	7.0		> 5
P	3.0	0.27	3.3

duces a ^{35}Cl resonance with a bandwidth which will be the weighted average of the two limiting numbers. Experiments have been devised, for instance, using mercurychloride (Hg-Cl)—labelling of proteins. When sodium chloride NaCl is reacted with mercuric chloride HgCl_2 , chlorine is present either as the chloride Cl^- or engaged in a covalent molecule:



Many macromolecules of biological interest have thiol (SH) groupings which react with

magnitude—upon addition of 10^{-5} M hemoglobin. When $14 \cdot 10^{-5}$ M Hg²⁺ is added to the solution the linewidth increases to 210 Hz. Therefore, as a rough estimate, the correlation time τ_c for the mercuric site on the hemoglobin is *ca* 100 times that of the free HgCl_4^{2-} :

$$\Delta\nu_{1/2} = K\tau_c \approx 210 \quad \text{hemoglobin}$$

$$\Delta\nu_{1/2} = K\tau'_c \approx 14,500 \quad \text{HgCl}_4^{2-}$$

assuming equal electrical field gradients q in the free HgCl_4^{2-} and in the bound state.

In such applications, it is often assumed that the quadrupolar nucleus exists only in either of two states, free (F) or bound (B). Then, if fast exchange prevails—which can be tested experimentally, for instance by checking that the linewidth is reduced upon increasing the temperature—the transverse relaxation rate $R_2 = T_2^{-1}$ can be expressed as the weighted average between the two limiting cases:

$$R_2(\text{obs}) = p_F R_{2F} + p_B R_{2B},$$

where p_F and p_B are mole fractions for the quadrupolar ion in the free and bound states, respectively. This amounts to using the relaxation rates as if they were simple coefficients, not bothering to analyze their various components and reduce the overall variation to a position in the binding equilibrium corresponding to the observed state.

There have been very many (self-avowed or implicit) applications of this methodology. We wish to single out especially the handsome work of the Lindman group. Many of the biological applications of the halide probes (Cl^- , Br^- , I^-), to the study of the binding of these anions to biomolecules such as the hemoglobins, are described in a concise and well-written book (Lindman and Forsén 1976).

4.3 The question of true complex formation

But how does one ascertain that binding truly occurs? One criterion that can be used is the usual test for complex formation (Laszlo 1980): a true complex is present if its lifetime exceeds the reorientational correlation time of the bulkiest part of the biomolecule, in the case of ion binding).

For instance, our Liège group has investigated during the last few years the binding of Na^+ cations by the apoproteins derived from calmodulins after treatment with EDTA or EGTA. The idea is to take advantage of the superior NMR properties of ^{23}Na compared to the ^{43}Ca nuclide for probing the vacant calcium-binding sites on these proteins. In every case we have studied, the correlation time τ_c descriptive of the ^{23}Na ions in the bound state has been found to be equal to the reorientational correlation time τ_R for the protein: τ_R is calculated from the Debye-Stokes-Einstein equation, $\tau_R = (V \cdot \eta / KT)$, where the protein molecular volume V is determined from the molecular density of the protein (table 18) (Grandjean and Laszlo to be published). This agreement, which is further supported by other results, such as the measured ^{23}Na quadrupolar coupling constants in the bound state, is consistent with the Na^+ -protein complexes being long-lived: the residence time τ_B of Na^+ in these complexes are (probably) greater by at least one order of magnitude to the

Table 18. Comparison between τ_c values for bound sodium ions and reorientational correlation times for the apoproteins derived from a number of calcium-binding proteins (Grandjean and Laszlo, to be published).

Calcioprotein (or fragment thereof)	MW	τ_c (nsec, ^{23}Na)	τ_R (nsec)
Bovine Gla protein	5700	2.5	2.6
Parvalbumin	11780	4.0	3.5
Phospholipase A2	14000	6	6.6
Tryptic fragment TR-1 from			
Troponin-C	8490	4.4	4.5
Troponin-C	17965	9.0	9.0
Tryptic fragment TR-1 from			
Calmodulin	8560	4.4	4.5
Tryptic fragment TR-2 from			
Calmodulin	8114	4.4	4.5
Calmodulin	16674	9.1	8.6
Crayfish MCBP protein	44000	19.2	20.6

4.4 Determination of the binding constants

When the biomolecular host offers n equivalent (or so-assumed) sites, the binding equilibrium is:



Variable concentration experiments provide K . For instance, trypsin hydrolysis cleaves troponin C—the molecule whose binding of Ca^{++} ions initiates muscular contraction—into two peptidic fragments, labelled as TR-1 and TR-2 (see table 18). TR-1, with residues 9-84, includes two 'low-affinity' calcium-binding sites, while TR-2, with residues 89-159, contains the two 'high-affinity' binding sites. With TR-1, it is observed that the ^{23}Na linewidth decreases monotonously upon addition of external Na^+ , in the form of aqueous sodium chloride, to a 1.45 mM solution of the apo TR-1 (figure 13). This decrease is simple to understand: in (34) the mole fraction p_F increases asymptotically towards unity. By combining these data with those from a titration curve in which the 'native' TR-1 is regenerated by addition of two equivalents of Ca^{++}

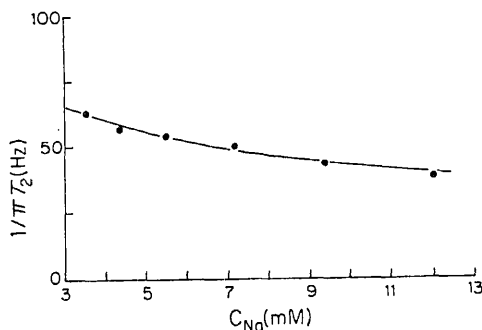


Figure 13. Plot of the observed half band widths $1/\pi T_2$ against the total sodium

ions (figure 14), it is possible by performing an iterative least-squares fit, to analyze the results for the binding constants K_{Na} and K_{Ca} descriptive of Na^+ and Ca^{++} binding. The results obtained thus by NMR ($K_{Na} = 91 \pm 15 \text{ M}^{-1}$; $K_{Ca} = (5.1 \pm 4) \cdot 10^5 \text{ M}^{-1}$) compare well with the literature values obtained by other methods, such as dialysis, for the low affinity sites in the whole troponin C molecules ($K_{Ca} = 3 \cdot 10^5 \text{ M}^{-1}$) (Delville *et al* 1980). The plot of figure 14 is also indicative of sodium-calcium competitive binding, at the low-affinity sites of troponin C, by contrast with the high affinity sites which feature a more complex phenomenon. The first bound Ca^{++} ion has a structural role, inducing the ordering of the protein from a rather random coil into a conformation with high helical content; this transition, seen by chiroptical methods, can also be followed by ^{23}Na NMR: with addition to TR-2 of 0-1 equivalent of Ca^{++} ions, sodium ions bind mostly to secondary sites, non-competitively with calcium ions (Delville *et al* 1980).

4.5 Determination of the rate constants for binding and release

In favorable cases, it is possible to go one step further, and to measure ultrafast rate constants using NMR (Laszlo 1980). The example we shall present here is that of gramicidin A, a pentadecapeptide with regular alternation of L and D residues, which spontaneously dimerizes in protic solvents such as water or methanol. Cell or vesicle membranes, doped with gramicidin A, when placed in aqueous medium containing univalent Na^+ and K^+ ions, have a time-dependent electrical conductance which was interpreted by Haydon (1972), as the diffusion of a sodium or potassium ion across the lipid bilayer. This diffusion occurs because of the lateral diffusion of the two halves of the bilayer, each containing some of these gramicidin A dimers. As a result, channels are formed, with lengths of 35–40 Å spanning the width of the bilayer and an inner diameter of 5–6 Å sufficient for inclusion of Na^+ or K^+ ions. Such channels exist for a time duration of the order of one second, as shown by the electric conductance experiments. In 1978, a German-Swedish group proposed, on the basis of a sophisticated mathematical analysis of electric conductance data, that each such channel, formed in gramicidin A-doped membranes, possesses two kinds of sites available to univalent cations: outer sites, at the entrance to the channel, right at the interface between the aqueous solution and the lipophilic membrane; and inner sites, buried in the lipophilic environment of the bilayer, separated from the outer sites by an energy barrier and also higher up in terms of potential energy (Neher *et al* 1978).

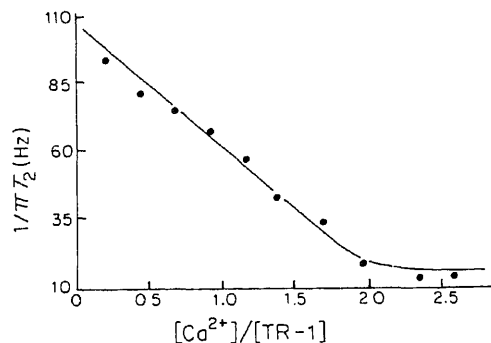


Figure 14. Plot of the ^{23}Na observed half band widths $1/\pi T_2$ against the $[Ca^{++}]/[TR-1]$

determined from ^{13}C longitudinal relaxation rates, is much longer, at $\tau_R \approx 30$ nsec (Fossel *et al* 1974). Since the correlation time τ_c is, in fact, a composite of the residence time τ_B at the binding sites, and of the reorientational correlation τ'_R for the complex ($\tau'_R \approx \tau_R$), the discrepancy between τ_c and the τ_R values shows that the correlation time τ_c :

$$\tau_c^{-1} = \tau_B^{-1} + \tau_R^{-1}, \quad (38)$$

is predominantly residence-determined. Hence, $\tau_B \approx 1.8$ nsec: since k_- , the rate constant for release of sodium ions by the gramicidin A dimers G_2 , is the reciprocal of this residence time τ_B , it is equal to $(5.5 \pm 0.5) \cdot 10^8 \text{ sec}^{-1}$. From variable concentration experiments, we determined separately the binding constant K appropriate for the equilibrium:



and found $K = 4.0 \text{ M}^{-1}$. Combining these two pieces of information yields a rate constant k_+ for binding, $k_+ = k_- \cdot K = (2.2 \pm 0.2) \cdot 10^9 \text{ M}^{-1} \text{ sec}^{-1}$; clearly, such a large value must come close to the diffusion-controlled limit; which is fully consistent with the notion of solvated Na^+ ions diffusing into the outer sites, which had been postulated on the basis of the conductance data (Corn  lis and Laszlo 1979). (Later on, the team of Prof. D. W. Urry, at the University of Alabama, were able to show, also using ^{23}Na NMR and working with G_2 units embedded in membranes, that inner sites are indeed also present; and that the ionic flows determined from NMR data are in order-of-magnitude agreement with those derived from the conductance data.) But there is yet an additional piece of structural information to be obtained from NMR: the quadrupolar coupling constant at the outer sites has the high value of 1.7 MHz, which is a sure sign of partial dehydration of the Na^+ ions in this bound state (Corn  lis and Laszlo 1979).

A multinuclear approach (^1H , ^{13}C , ^{23}Na , ^{31}P , ^{39}K , ^{87}Rb) has been employed to study 5'-guanosine monophosphate (5'-GMP) aggregation in aqueous solutions (Borzo *et al* 1980; Detellier and Laszlo 1980; Delville *et al* 1979; Detellier and Laszlo 1979). 5'-GMP self-orders at neutral and slightly basic pHs by a process which depends critically on the cation present (Detellier *et al* 1978; Paris and Laszlo 1978; Pinnavaia *et al* 1978). It was shown that in presence of sodium cations only, 5'-GMP aggregates by dimerization of planar tetramers, followed by dimerization of octamers in hexadecamers (40):



The residence time of a sodium cation on the octamer was in the range of 20–60 nsec, whereas the nucleotide counterions exchange with much slower rate constants, of less than 10^2 sec^{-1} , as was shown previously by ^1H NMR (Pinnavaia *et al* 1975). Observation of such residence times ($\tau_B \approx 30$ nsec) rules out conclusively sodium binding to a single phosphate, and is consistent only with sodium binding by several groups. Recent

determinations of the crystallographic structures of disodium GMP heptahydrate show that the sodium coordination shells involve no direct interactions with the ionized phosphate groups but coordination by N(7) of the guanine base or by O(2') or O(3') of the sugar moiety (Barnes and Hawkinson 1982; Katti *et al* 1981). The value of the limiting chemical shift of ^{23}Na in the aggregate was in the range of -100 to -160 ppm and indicated coordination with atoms of strongly different types: O_6 oxygens or guanine nitrogens (Borzo *et al* 1980). A conclusion is to be strongly emphasized: sodium cation binding contributes directly to the buildup of octamers and hexadecamers.

The self-ordering process requires lower concentrations of $5'\text{-GMP}$, 2Na^+ when potassium ions are present (Detellier *et al* 1978). Comparison of K^+ with the other alkali metal cations shows a marked selectivity favouring potassium, with the sequence $\text{K}^+ > \text{Rb}^+, \text{Na}^+ \gg \text{Li}^+, \text{Cs}^+$ being observed (Pinnavaia *et al* 1978).

We found a single correlation time of 9.4 nsec characterizing the aggregates in the presence of potassium, to which we attributed the composition ($\text{G}_8, \text{K}^+, 4\text{Na}^+$). It is a species to which the Na^+ ions are tightly and durably bound, which is formed with cooperativity. The model we proposed is based on coexistence of two kinds of sites, inner site selective toward potassium ions and outer sites that display a strong apparent preference for sodium ions over potassium or rubidium ions. This remarkable self-assembly, unlike a normal stacking interaction, is not determined predominantly by hydrophobic forces, but by cation binding. The self-assembly is enthalpy-driven, since the entropy change upon self-association is strongly negative ($\Delta H = -22 \pm 3 \text{ kcal mol}^{-1}$; $\Delta S = -58 \pm 7 \text{ cal mol}^{-1} \text{ K}^{-1}$) (Detellier and Laszlo 1980).

Recent studies of those self-associates using low-frequency Raman scattering techniques supported the conclusion that the potassium ion is enhancing the self-association as compared to the sodium ion (Nielsen *et al* 1982), and recently also Fisk *et al* (1982) have shown by ^1H and ^{13}C NMR that the most stable species formed in the self-association of Na_2 $5'\text{-GMP}$ is a head-to-tail octamer, formed by the association of two tetrameric plates.

4.6 Isomorphous replacement technique

In preceding sections (4.1 and 4.4), we have already drawn attention to the competitive binding of sodium and calcium ions. Indeed, both Na^+ and Ca^{++} share an identical ionic radius of $0.95 \text{ \AA}$, so that sodium ions are good probes for the binding of calcium ions (Phillips and Williams 1966). This is an example of an isomorphous replacement. As implied by the entries in table 17, we have been able to use this technique to monitor the metal binding sites of a number of calceins, after partial or total decalcification, by the tactic of Na^+ probes, taking advantage of the higher sensitivity of ^{23}Na , as compared to ^{43}Ca NMR.

One crucial question remains: how can we tell that true binding does indeed take place? As indicated above, the equality $\tau_c = \tau_R$ for the sodium ions in the bound sites, allowed us to answer it in the affirmative (table 17). A test case is that of the bovine Gla protein, a small ($M = 5,700$) 49 residue molecule, capable of binding three Ca^{++} ions per molecule at its three Gla (γ -carbonyl-glutamic acid) residues, in positions 17, 21 and 24. It is a limiting case because the calcium binding constant is quite low: $K_d \approx 3 \text{ mM}$. Hence, since *a priori* the electrostatic binding energy of univalent sodium ions should be approximately half that for the divalent calcium ions, binding constants for sodium

example, the isomorphous replacement method worked, as indicated in table 17 (see also Grandjean and Laszlo 1982). Thus exploration in calceproteins of calcium-binding sites with $^{23}\text{Na}^+$ ions appears to be a rather general and useful method.

5. Interaction between ions and polyelectrolytes

In this last section, we consider very briefly a special case of ion-molecule interaction, when the molecule itself is an ion, or rather a poly-ion. Hence, such interactions when the species involved bear electrical charges of opposite signs, come under the province of ion pairing phenomena. When each charged site on the poly-ion behaves independently of its neighbours, the binding of the counterion can be described in the usual manner, as a chemical equilibrium, and the formalism is similar to that in the preceding section (see especially (36), where p_n would correspond now to the mole fraction of *tight* or *intimate* ion pairs). This first mode of attachment between polyelectrolyte and its counterion is termed *site binding*.

A different mode of interaction sets in when the distance between adjoining charged sites on the polyion decreases to a (critical) value and condensation of the counterions occurs in order to reduce the charge density of the polyelectrolyte. One can view this phenomenon also as a screening, by the counterions, of the Coulombic repulsion between adjacent charged sites, when these become too close to one another. This second mode of ionic attachment to a polyelectrolyte is termed *atmospheric condensation*. Its equivalent, for monomers, would be a *loose* or *solvent-separated* ion pair. In atmospheric condensation, a distribution of the fully-solvated counterions is set up, in the vicinity of the polyelectrolyte, so that they congregate near the poly-ion, trapped radially but not tangentially in its electrostatic potential. There are basically two kinds of theoretical treatments of atmospheric condensation, either through solution of the Poisson-Boltzmann equation, or through simplified two-states counterion condensation models; since these theories have been reviewed adequately quite recently (Anderson 1982), in their application to the linear topology of a rod-like polyelectrolyte, we shall limit our remarks here to discussion of a few NMR results.

With the classical Poisson-Boltzmann equation, an analytical solution is completely equivalent to a numerical solution (Delville *et al* 1982). However, the classical Poisson-Boltzmann treatment suffers from its assumption of point charges, and from the neglect of interionic correlation. It has been shown, using a cell model in which the cylindrical volume around each polyelectrolyte molecule is divided into a series of coaxial cylindrical shells, that a modified Poisson-Boltzmann equation accounts extremely satisfactorily for both the activity coefficients measured electrochemically, and for the observed ^{23}Na NMR line broadenings, when aqueous solutions of sodium polystyrenesulfonate are studied in the presence of various added salts—such as NaCl, KCl, CaCl_2 , MgCl_2 or MnCl_2 (Delville *et al* 1982). The modifications to the classical Poisson-Boltzmann equation consist: firstly, in a realistic choice of the radius of the first shell, chosen equal to the diameter of the solvated counterions; and, secondly, in a semi-

al 1982). But the application to the observed ^{23}Na NMR line broadenings, due to the presence of the polyelectrolyte, is yet more interesting. One will recall that, for the quadrupolar $^{23}\text{Na}^+$ ions ($I = 3/2$), the linewidth should be (under extreme narrowing conditions) proportional to the average value of the squared electric field gradient at the nucleus $\langle q^2 \rangle$, multiplied by a correlation time τ_c descriptive of the fluctuations in time of this electrostatic field gradient. From what was said above, atmospherically-condensed ions retain their full solvation sphere, together with two of their three degrees of translational freedom, and their three degrees of rotational freedom. To a very good approximation, they can be assumed to be describable by a single correlation time which, probably, is much closer to that of the free ion than to the reorientational correlation time of the polyelectrolyte. Indeed, when the observed line broadenings, after being normalized to the same amount of atmospheric condensation, are plotted against $\langle q^2 \rangle$, a nice linear regression (going through the origin) ensues, with a slope giving order-of-magnitude agreement with the Sternheimer anti-shielding coefficient ($1 + \gamma_\infty$) for the isolated Na^+ ion (after correction for polarization by the water molecules in the solvation sphere of the atmospherically condensed Na^+ ions) (Delville *et al* 1982):

If one is interested only in accounting quantitatively for the NMR results—in isolation from, say, activity coefficients—a full Poisson-Boltzmann treatment is not an absolute necessity. This is because the calculated electrostatic field gradient is determined overwhelmingly by the contribution for the counterions present in the first shell, right next to the polyelectrolyte. Hence, a two-states treatment, such as that of Manning, or that of Guéron and Weisbuch (see the review of Anderson (1982) for a detailed presentation), will perform satisfactorily. We have even found, in re-examining the results we had obtained a few years ago on sodium heparinate (Herwats *et al* 1977), that the chemical equilibrium model (site binding) we had resorted to in their interpretation, while being conceptually much less satisfying than the notion of atmospheric condensation, differs only semi-quantitatively from the results of the more rigorous modified Poisson-Boltzmann treatment. This is also because, from the point of view of the NMR observables, these results depend quasi exclusively on the *local* contributions for condensed ions in the immediate vicinity of the polyelectrolyte; hence it is possible to lump together all of the other condensed ions, which are virtually unaffected in their NMR properties, *as if* they were free ions (which of course they are not really!) (Delville and Laszlo 1983).

Ordered poly-ions such as sodium heparinate play an important role in biology: DNA is the prime example; its interactions with, especially Mg^{++} ions, are of crucial importance in determining its state in biological systems. Thus, ^{25}Mg NMR has been applied to a study of magnesium ion interactions with DNA (Rose *et al* 1980): site-binding magnesium interactions are important even at moderate concentrations of the ions, which is in contrast with the type of fixation of sodium, mainly atmospheric (Anderson *et al* 1978). The applicability to DNA of the considerations outlined above is the main reason for the considerable current interest in polyelectrolyte theories, and their application to counter-ion binding or condensation (Anderson 1982).

the entire landscape of ion-molecule interactions, we have elected to delve on those areas with which we are more familiar. Conversely, we regret that—this review being by necessity of paper—rather than of book-length—we have had no room for discussion of many important topics.

These include important questions such as:

(i) the shielding of ions from a lipophilic environment, using appropriate molecular ligands, such as crown ethers and cryptands for selective extraction into organic solvents, or ionophores for ionic transport across membranes; this type of ion-molecule interaction, while very important to chemists and biochemists, has not yet been addressed directly using NMR methods.

(ii) the conformational changes induced, in solution, on the molecular ligands by the binding of ions; this phenomenon has been studied extensively by NMR, in laboratories such as those of Prof. M J O Anteunis, at the University of Ghent, and of Dr. J Y Lallemand, at the Ecole Normale Supérieure, in Paris. It is obviously connected with the question of the geometries for ionic coordination.

(iii) likewise, there has been no room here for discussing changes in molecular electronic distributions, as can be studied from *e.g.* ^1H and ^{13}C chemical shifts, upon ion binding; nor for studying the type of interaction present between an ion and a molecule (charge control *vs* orbital control, in the Klopman distinction; electrostatic versus covalent, a distinction which is extremely relevant to *e.g.* the binding of Li^+ ions).

(iv) NMR methods *can* be used for determining the heat of formation of ion-molecule complexes in solution, and comparing them with their calorimetric, or gas-phase values (the latter obtained for instance by the astute mass spectrometric methods pioneered by Prof. Kebarle).

(v) likewise, we have skipped completely the chemically-interesting topic of Lewis acidities and basicities in solution, and with reference to their gas phase values.

(vi) and we have been forced to neglect, not for lack of interest but for lack of space, miscellaneous topics such as quaternary ammonium ions and the hydrophobic effects associated with these when they include long hydrocarbon chains; the validity of the so-called extra-thermodynamic assumptions; etc.

Finally, as we had already made clear in the introduction, we have written this account from a somewhat bio-inorganically biased perspective, choosing to emphasize interactions between metal ions and organic molecules, since more classical topics such as the ion pair separation of salts formed by organic anions and cations have already received ample coverage in the literature.

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Nuclear spin relaxation and intermolecular interactions

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1. Introduction

In order to specify what kind of information about intermolecular interactions can be obtained by nuclear spin relaxation, we consider a suitable microscopic representation of a liquid. For reasons which will become clear below, this article is entirely confined to the treatment of the liquid phase. The molecular or microscopic picture of a liquid may be considered to be a system consisting of very many mass points being separated in space. Thus, if there are N mass points, we have at each instant N positions $\mathbf{r}_i$ which are all different from each other. These positions are changing with time and thus $d\mathbf{r}_i/dt \neq 0$, which means that each mass point is also characterized by an instantaneous velocity.

Generally, the motion of the mass points, $\mathbf{r}_i(t)$, is uncorrelated, that is, if $\mathbf{r}_i(t) - \mathbf{r}_i(0)$ represents the displacement vector of the i th mass point after a time t , then the displacement vector of another mass point j , $\mathbf{r}_j(t) - \mathbf{r}_j(0)$, may have any value. Thus the change with time of the vector pointing from one mass point to the other, $\mathbf{r}_j - \mathbf{r}_i$, can be described as an ordinary relative random diffusion process. However, for certain pairs of mass points i, j we observe correlations of the motion, the most important forms of correlations are those for which $|\mathbf{r}_j - \mathbf{r}_i|$ remains unchanged with time, or in other words, the distance between two mass points—apart from vibrational motions—is a constant quantity. Of course, such correlations are characteristic for intramolecular vectors connecting two atoms.

Furthermore, the mass points have another property, they are 'named mass points' in the sense that they represent a certain chemical substance, or, briefly expressed, they have a well defined position $\mathcal{R}_j$ in the two-dimensional coordinate system which is called the periodic table of the elements. In contrast to the positions in ordinary space, $\mathbf{r}_i$, the mass points may have partly the same positions $\mathcal{R}_j$ in the element space, even more than this, in a liquid element all mass points are at the same $\mathcal{R}_j$. For all systems of "reasonable" composition, and those are the systems to be treated here, the number of occupied positions $\mathcal{R}_j$ in element space is small ≤ 10 , say.

Now we consider a *molecule* as being a set of 'named' mass points. As will be seen below, it is not a simple matter to define a molecule in a liquid on a microscopic level. However let us postulate that the molecule is well defined by some macroscopic analytical or chemical operation. Here it is sufficient to require that within the molecule at least partly there exist strict distance and possibly also angular correlations between the mass points (atoms) which allow the construction of a three-dimensional

we will find that the origin of the coordinate system of the second molecule is located at $\mathbf{r} \equiv \mathbf{r}_{12}$ with respect to the coordinate system in the first molecule. Let the relative orientation of the two molecules (rigid body coordinate systems) be given by the set of three Eulerian angles, Ω . Then the potential energy *in vacuo* of this pair as a function of $\mathbf{r}$ and Ω ,

$$E = E(\mathbf{r}, \Omega), \quad (1)$$

we denote by the *intermolecular interaction energy*. It should be emphasized that this concept refers to the isolated pair of molecules, thus the operational definition of $E(\mathbf{r}, \Omega)$ involves the separation of the molecular pair from the bulk of the liquid and transferring it into the extremely diluted gas phase. Furthermore, we have already indicated that in many cases the molecule is not a rigid body, it may exist in several conformations, then we would have an intermolecular interaction energy

$$E = E(\mathbf{r}, \Omega, \alpha), \quad (1a)$$

where α characterizes any appropriate internal degree of freedom which is virtually independent of $\mathbf{r}$ and Ω .

A special form of intermolecular interaction is the H-bond. For the treatment to be given below it is convenient to present a definition of the H-bond here. We select from the totality of molecules those which contain an H atom being separated by $\approx 1 \text{ \AA}$ from one of the atoms O, N, F (C only in exceptional cases, *eg* CCl_3H). Then again, formally (1) or (1a) constitute what we call a hydrogen bond. The classification of an intermolecular interaction to be a H-bond may also be confined to a certain range or interval of $\mathbf{r}$ and Ω , which would more strongly emphasize the character of a bond, but this is merely a matter of convention. Now, if we have an H-bond, $E(\mathbf{r}, \Omega)$ has some particular features. We quote four which seem to be the most important ones. (1) $E(\mathbf{r}, \Omega)$ certainly contains some electrostatic admixtures, the one of lowest multipole character being the electric dipole-dipole interaction. (2) If we choose the zero of $E(\mathbf{r}, \Omega)$ at very large separation, then the minimum value of $E(\mathbf{r}, \Omega)$ is lower than that found for other molecules of comparable mass and composition. (3) The separation of the minimum for the potential energy from the hydrogen atom is particularly small, such that the distance between the oxygen or corresponding other atoms is $\leq 3.4 \text{ \AA}$ and $\geq 1.7 \text{ \AA}$, (4) finally, the H-bond has the following peculiarity: Assume for a moment that all other atoms apart from those H's having a distance $\approx 1 \text{ \AA}$ from O, N, or F constitute a rigid molecule. Let the intramolecular positions of one of these atoms be $\mathbf{r}_{1i}$, $i = 1, 2$, where $i = 1, 2$ means: in the first and second molecule, respectively. Then we may investigate the potential energy function

$$E^* = E^*(\mathbf{r}, \Omega, \mathbf{r}_{11}, \mathbf{r}_{12}),$$

i.e. we take the potential energy as a function of $\mathbf{r}$, Ω , and the two atomic positions $\mathbf{r}_{11}$, $\mathbf{r}_{12}$. The result will be that the dependence of E^* on $\mathbf{r}_{11}$ and $\mathbf{r}_{12}$ is virtually independent of $\mathbf{r}$ and Ω . Next we select the H-atoms adjacent to the N, O, or F, let their intramolecular positions be $\mathbf{r}_{\text{H}1}$, $\mathbf{r}_{\text{H}2}$ (if there is only one such H-atom per molecule, otherwise we have to add one more index). We investigate again the potential energy

The region of $\mathbf{r}$ and Ω for which (3) is valid defines the H-bond in a narrower sense.

The following two things will have become clear from the description of the liquid system given so far:

(1) We wish to apply nuclear spin relaxation with the aim of obtaining information about $E = E(\mathbf{r}, \Omega)$.

(2) $E = E(\mathbf{r}, \Omega)$ is a continuous function in six-dimensional space, so it will certainly not be possible to get complete information about $E(\mathbf{r}, \Omega)$, the information has to be a truncated one. Moreover, as we have seen, $E = E(\mathbf{r}, \Omega)$ is defined as a property of an isolated molecule pair *in vacuo*, it raises the question of which of the properties of $E(\mathbf{r}, \Omega)$ is preserved if we merge the pair of molecules in the bulk of the liquid, the object of our experimental procedures.

A rigorous and general answer to the latter question cannot be given. However, in principle the answer should come from the calculation of configurational distribution functions. To characterize the situation, let us return to the assembly of named point masses representing the microscopic picture of the liquid. It is a postulate of the atomistic description of matter that—at least in classical systems—a microscopic observer can perform measurements of the positions $\mathbf{r}_i$ of the particles. From our knowledge of the nature of the system we can, in principle, make predictions of the probability that the microscopic observer finds certain positions. These predictions involve the laws of classical mechanics together with the particular reasoning of statistical mechanics. It is fairly clear that the probability of finding any mass point (atom) of kind k at a given position $\mathbf{r}$ is $N_k/V \cdot d\mathbf{r}$ where N_k is the total number of particles of type k and V is the volume of the system. One sees that this probability is independent of the system. However, if we ask what the probability is of finding a second atom at $\mathbf{r}$ relative to the first one, it can only be independent of $\mathbf{r}$ if the atoms considered are far apart. At smaller separations, the probability $p(\mathbf{r})d\mathbf{r}$ is distance dependent. Furthermore, as we saw when the molecules can be considered to be rigid bodies or partly rigid bodies, then a pair of molecules is not only characterized by the vector $\mathbf{r}$ pointing from the origin of one intramolecular coordinate system to that in the other one, the relative orientation has also to be given. Then we may ask what is the probability density $p(\mathbf{r}, \Omega)$ for the microscopic observer of finding a pair of molecules being characterized by the set of quantities $\mathbf{r}$ and Ω . For this probability density we can formally write:

$$p(\mathbf{r}, \Omega) = \frac{N}{V 8\pi^2} \exp[-\tilde{E}(\mathbf{r}, \Omega, T)/kT], \quad (4)$$

where N is the total number of molecules in the system, the probability distribution of which we wish to predict or to study. The exponent is dimensionless, thus the quantity $\tilde{E}(\mathbf{r}, \Omega, T)$ must be of the dimension of energy. Since in general the left-hand side of (4) is unknown, $E(\mathbf{r}, \Omega, T)$ represents nothing more than a transcription of the unknown function $p(\mathbf{r}, \Omega)$ into the function $\tilde{E}(\mathbf{r}, \Omega, T)$, consequently $\tilde{E}(\mathbf{r}, \Omega, T)$ is also an unknown function. $\tilde{E}(\mathbf{r}, \Omega, T)$ is designated as the potential of mean generalized forces for reasons which cannot be explained in detail here. The question arises: what is the relation between $E(\mathbf{r}, \Omega)$ as given by (1) and $\tilde{E}(\mathbf{r}, \Omega, T)$ occurring in (4)? It is obvious that $\tilde{E}(\mathbf{r}, \Omega, T)$ is some kind of superposition of all the effective interactions in the liquid to

yield the occurrence probability for a certain pair of configurations. The superposition involves the temperature because in some way the relevant distributions are governed by the temperature. In contrast to this, $E(\mathbf{r}, \Omega)$ does not contain a temperature dependence, it is defined in connection with one isolated particle pair *in vacuo* where the temperature has no physical meaning. Now, the only possibility for us to make any progress at all towards the aim we have envisaged is to set

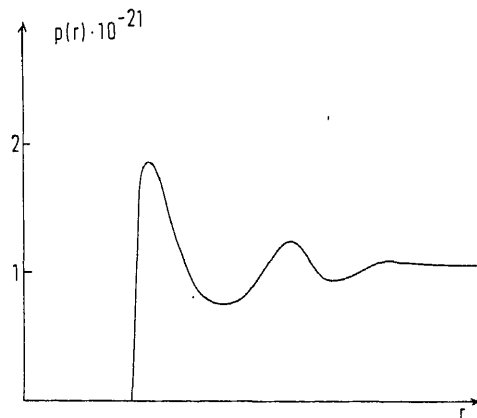
$$E(\mathbf{r}, \Omega) \approx \tilde{E}(\mathbf{r}, \Omega, T) \quad (5)$$

In general the justification of this approximation may be very doubtful, there may be cases where $E(\mathbf{r}, \Omega)$ is much larger than $\tilde{E}(\mathbf{r}, \Omega, T)$, perhaps twice as large, this will probably be the case if we have fairly long range intermolecular interactions, as in the presence of hydrogen bonds as we have already mentioned. In principle, of course, within the framework of statistical mechanics $\tilde{E}(\mathbf{r}, \Omega, T)$ should be fully determined by $E(\mathbf{r}, \Omega)$, however, the relevant equations connecting these two quantities, even if we postulate that they are known, are mathematically very complicated. As will be shown below, as approximate as it may ever be, (5) represents the first link between the intermolecular interaction energy and the nuclear magnetic relaxation process.

The information contained in (4) can be reduced by an averaging procedure with respect to the orientation. We once again consider the atom k which is one of the constituents of the molecule in question. Assume that we have a particular pair configuration in which the intermolecular distance between the atoms k is r_{kk} . Now we average over all orientations Ω and $\mathbf{r}$ values which are compatible with r_{kk} . This averaging procedure must also be done for all directions of r_{kk} with respect to the intramolecular reference system. The result is the k - k atomic pair distribution function

$$p(r_{kk}) = \frac{N_k}{V} \exp[-\tilde{E}(r_{kk}, T)/kT] \quad (6)$$

a quantity which is well-known, in particular from the evaluation of x-ray, neutron, and electron scattering experiments. It gives the probability density of finding the atom k at a distance r_{kk} anywhere around the reference atom k . A typical representation of $p(r_{kk})$ is given in figure 1 (see *e.g.* Egelstaff 1967; Hansen and McDonald 1976; Kohler 1972; Croxton 1975). Now in the light of (6) the intermolecular interaction



seems to be smeared out spherically symmetric around the reference atom. In such a situation the intermolecular interaction energy seems to be a quantity which only depends on the mutual separation of the atom in question. It should be noted that in x-ray and electron scattering experiments—apart from other fundamental problems—difficulties occur when there are several atoms of kind k in the molecule, since the requirement that (6) tells us something about the intermolecular interactions is never fulfilled. In nuclear magnetic relaxation experiments the situation is more favourable because the isotopic substitution techniques can be applied in many cases to distinguish between inter- and intramolecular interactions. In a more restricted sense isotopic substitution is also helpful in performing and analyzing suitable neutron scattering measurements (see e.g. Enderby and Neilson 1979). Details of the isotope substitution method will be given below. Thus in a quite general sense, for the nuclear spin relaxation studies to be described here (6) is a fairly basic relation, however, in order to be connected with direct experimental results it has to undergo a further simplifying process, thus the information available is much more limited as will become clear below.

In order to proceed further, at the moment it is convenient to consider (6) as an immediate result to which we shall return later and go back once again to the microscopic model of the liquid as being a system of 'named' mass points in which both configurational and motional correlations exist.

We have now to direct our attention to the fact that some of the mass points may possess an intrinsic angular momentum, the nuclear spin, and connected with it a magnetic moment. Whether the atom has a nuclear moment or not depends on the particular isotopic species which it represents. So far we did not mention the electronic environment surrounding the mass points. Indeed, for the most important physical facts we are concerned to describe, it suffices to consider the atoms as being simple named mass points, independent of the nuclear spin variable; and certain further specification of the isotopic environment in some cases is necessary, however, for other types of experiments where it is needed to take into account the electron cloud indirectly because it may produce an electric field gradient at the nuclear site. If the nucleus has a spin $I > \frac{1}{2}$, it will also have an electric quadrupole moment which interacts with the electric field gradient. Only occasionally we shall meet a situation where the electron cloud as well has an intrinsic angular momentum, the electron spin—again this spin is connected with a magnetic moment.

The sum of all nuclear magnetic moments, of course, is a macroscopic property of the liquid and thus it must be an observable, otherwise there would be no reason to speak of nuclear magnetic moments. If we refer the sum of all these nuclear moments to unit volume, we have the nuclear magnetization, M , of the liquid in question. It is clear that in every thermodynamic equilibrium the observable mean value of the magnetization is constant. However, in the presence of an external magnetic field the nuclear magnetization does not vanish and if we apply external magnetic fields which are time dependent, then in general the nuclear magnetization will also vary with time; thus we have to consider the three components of the nuclear magnetization

the desired information about the intermolecular interaction relevant for the liquid in question. $1/T_1$ and $1/T_2$ are called the longitudinal and transversal relaxation rates, respectively, and describe the change with time of the components of $\mathcal{M}$ in the case that the external magnetic field is independent of the time (Abragam 1961; Farrar and Becker 1971; Slichter 1980). Then if at any instant we have $\mathcal{M}_x, \mathcal{M}_y, \mathcal{M}_z \neq 0$, $1/T_1$ and $1/T_2$ are defined by the relations

$$\frac{d\mathcal{M}_z}{dt} = \frac{1}{T_1} (\mathcal{M}_z^0 - \mathcal{M}_z), \quad (7)$$

$$\frac{d\mathcal{M}_x}{dt} = -\frac{1}{T_2} \mathcal{M}_x, \quad \frac{d\mathcal{M}_y}{dt} = -\frac{1}{T_2} \mathcal{M}_y, \quad (8)$$

where $\mathcal{M}_z^0$ is the equilibrium magnetization in the presence of the static field, the two equations containing $1/T_2$ are referring to the transverse components of $\mathcal{M}$ measured in a coordinate system which rotates with the nuclear magnetic resonance frequency.

Now let us return to (6). It may be seen that $p_{kk}(r)$, or more generally, $p(r)$, does not contain the time, it is an equilibrium property which of course is time independent. On the other hand, the macroscopic quantity $\mathcal{M}$ we are observing is a time dependent quantity, it is the movement towards equilibrium with which we are concerned. Thus it is natural to expect that the observables $d\mathcal{M}_i/dt$, $i = x, y, z$, are not primarily determined by the time independent $p(r)$. There must be some internal microscopic motion which causes or produces the macroscopic change with time. In fact, it is the motion of the mass points carrying the nuclear magnets which makes $d\mathcal{M}_i/dt \neq 0$, and in particular, it is the fluctuating nuclear magnetic interaction energy (or quadrupole interaction energy) between the mass points which is important. From this insight it will be immediately clear that the only thing which is relevant for us is the relative motion of a given mass point with respect to another one, of course then the total effect comes from the superposition of all the fluctuating pair interactions.

It is important to clarify the term 'interaction energy' here, because it occurs in two different senses. First we have the intermolecular interaction $E = E(\mathbf{r}, \Omega)$ between the molecules which causes the particular structure of the liquid. Then secondly we have the interaction energy between the nuclear magnets (or between the nuclear quadrupole moments and the electric field gradients) which we may denote by $V(\mathbf{r})$ where now the vector $\mathbf{r}$ connects the two nuclei—or the reference nucleus with a representative site of the source of the field gradient. $V(\mathbf{r})$ does not at all influence the structure of the liquid because we have $V(\mathbf{r}) \ll E(\mathbf{r}, \Omega)$. Thus the interaction energy $V(\mathbf{r})$ is essentially applied to probe the intermolecular energy we wish to study. After these introducing remarks it will be understandable that the microscopic quantity we need in order to link it with the macroscopic observable is the motion of one mass point relative to the other one, and this property is described by the quantity $\mathcal{P}(\mathbf{r}_0, \mathbf{r}, t)$ which is the microscopic density self-correlation function of atom 2 relative to the atom 1. Expressed in another way, $\mathcal{P}(\mathbf{r}_0, \mathbf{r}, t)$ is the probability density of finding at time $t = 0$ a given atom—here numbered as atom 2—at $\mathbf{r}_0$ relative to another atom—here numbered as atom 1—and of finding the same atom 2 at time $t = t$ at $\mathbf{r}$ relative to atom 1. It is clear that in general $\mathcal{P}(\mathbf{r}_0, \mathbf{r}, t)$ as a full function of the three variables $\mathbf{r}_0$, $\mathbf{r}$, and t is not available, this is the same situation as we had found it for the two time-independent probability distribution functions we have discussed so far. However, for the readers convenience, it should be

stated that one limiting form of $\mathcal{P}(\mathbf{r}_0, \mathbf{r}, t)$ which can immediately be written down is

$$\mathcal{P}(\mathbf{r}_0, \mathbf{r}, t) = c' [4\pi(D_1 + D_2)t]^{-3/2} \exp[-(\mathbf{r} - \mathbf{r}_0)^2/4(D_1 + D_2)t], \quad (9)$$

if $\mathbf{r}_0$ is very large compared with the radius r_2^* of the second coordination sphere of atom 1. r_2^* is defined by the location of the second minimum of the 1-2 pair distribution function, c' is the number density of the atom 1 and D_1 and D_2 are the self-diffusion coefficients of the molecules carrying the atom 1 and 2, respectively, and the factor of c' in (9) is the appropriate solution of the ordinary diffusion equation.

From the inspection of (9) it is directly suggested that in the general case we may write for $\mathcal{P}(\mathbf{r}_0, \mathbf{r}, t)$

$$\mathcal{P}(\mathbf{r}_0, \mathbf{r}, t) = p(\mathbf{r}_0)P(\mathbf{r}_0, \mathbf{r}, t), \quad (10)$$

where $P(\mathbf{r}_0, \mathbf{r}, t)$ is very often called the 'propagator', it is the joint probability density of finding at time t atom 2 at $\mathbf{r}$ relative to atom 1 if it is known that at $t = 0$ the relative location of 2 was $\mathbf{r}_0$, $p(\mathbf{r}_0)$ is the radial pair distribution function with respect to the pair of atoms 1 and 2 and is exactly the quantity we have given as (6). There we had considered the special case that the vector $\mathbf{r}$ connects two atoms of kind k , here the atoms 1 and 2 may be of any kind, either different or the same; the subscript 0 was not needed in (6) because time did not enter the picture. If we are not explicitly interested in the time development, we shall again omit the subscript 0 in the following.

The macroscopic movement of the nuclear magnetization of course must involve a time integral over $\mathcal{P}(\mathbf{r}_0, \mathbf{r}, t)$, moreover due to the nature of the system, we can only be concerned with an integration over all pair configurations, thus an expression

$$\int_0^\infty \left(\int p(\mathbf{r}_0) P(\mathbf{r}_0, \mathbf{r}, t) d\mathbf{r}_0 d\mathbf{r} \right) dt,$$

enters the microscopic theory. Finally, as was already mentioned, the nuclear interaction $V(\mathbf{r})$ must also occur in the expression determining the time dependence of the magnetization, thus we arrive at the expression

$$\int_0^\infty \exp(-i\omega t) \left\{ \int p(\mathbf{r}_0) V(\mathbf{r}_0) V(\mathbf{r}) P(\mathbf{r}_0, \mathbf{r}, t) d\mathbf{r}_0 d\mathbf{r} \right\} dt, \quad (11)$$

where ω is the nuclear magnetic resonance frequency, the factor $e^{-i\omega t}$ reminds us that we have to do with a resonance phenomenon in which in some way transitions from one state to another are of importance. As will be seen below, expressions of the type (11) have to be evaluated in order to get information about $p(\mathbf{r}_0)$ from spin relaxation data. Indeed, the reader will agree that the access to the intermolecular interactions *via* the study of nuclear magnetic relaxation is only a very indirect one. And one fact which we have not mentioned yet should not be overlooked, namely, that the propagator $P(\mathbf{r}_0, \mathbf{r}, t)$ is also determined by the same intermolecular potential $E(\mathbf{r}, \Omega)$ which determines $p(\mathbf{r})$. Thus, in order to obtain the very limited information about $p(\mathbf{r})$, in the ideal case it is supposed that $P(\mathbf{r}_0, \mathbf{r}, t)$ which is determined by the same intermolecular forces, is already known. This is of course a presupposition which is never fulfilled.

At the end of the introduction it should be mentioned that the translational motion can directly be studied by an NMR technique. Spin-echo methods (Abragam 1961) allow the measurement of the self-diffusion coefficient. The dephasing of transversal

sample region in this second process enables a direct evaluation of D . These are the quantities occurring in (9), both the single values D_1 and D_2 can be measured in favourable cases. The value of D of one special chemical system can be discussed by comparing it with the D of a suitably chosen reference state. Intermolecular interactions result in characteristic changes. To give an example we expect a slowing-down of the translational motion for a system forming higher aggregates. The determination of D will be a great aid in the interpretation of the nuclear magnetic relaxation rates.

Two final comments should be added. There is, in general, no other method which in a clear cut way gives better information about $E(\mathbf{r}, \Omega)$ or $\dot{E}(\mathbf{r})$ in molecular liquids. Secondly, in solids $P(\mathbf{r}_0, \mathbf{r}, t)$ or $\mathbf{r} \neq \mathbf{r}_0$ in most cases is a very small quantity, therefore the methods of description and evaluation we present in this article do not apply to solid state NMR investigations. In the solid the intermolecular interactions are manifested by the respective distances in the crystal structure (Schuster *et al* 1976) or by the kind of the vibrational motion (Anderson *et al* 1973). If there are molecular motions in the solid leading to nuclear magnetic relaxation processes, then these motions mostly are also determined by intramolecular forces, only in a few cases does the whole molecule perform a rotational motion and thus reflect intermolecular interaction alone (see *e.g.* Walker 1980). Although solid state NMR can yield certain information about intermolecular forces, for reasons of room the respective topics will be omitted in this article (Mehring 1976; Spieß 1978b; Owens *et al* 1979).

2. The intermolecular relaxation rate

2.1 Some introductory remarks

We have considered a system consisting of N molecules, each of them carrying n nuclear (or electron) spins. Then the total relaxation rate $1/T_1$ of the nuclear spin system is caused by the magnetic interaction of each of the nuclei with $n-1$ nuclei in the same molecule and $(N-1)n$ nuclei in other molecules. $1/T_1$ is defined by (7). Thus, in general $1/T_1$ has to be separated into two contributions denoted as intra- and intermolecular relaxation rates, $(1/T_1)_{\text{intra}}$ and $(1/T_1)_{\text{inter}}$ (Abragam 1961; Hertz 1967a)

$$\frac{1}{T_1} = \left(\frac{1}{T_1} \right)_{\text{intra}} + \left(\frac{1}{T_1} \right)_{\text{inter}}. \quad (12)$$

According to the programme given in the introduction, the systems under consideration will be liquids in all cases. It was already indicated that the denotations intramolecular and intermolecular are not without problems, this requires a definition of a 'molecule' in the liquid phase. In the gaseous phase a molecule may be defined by the respective equations of state, as *e.g.* by the relation $pV = (m/M)RT$. In the liquid state intermolecular interactions may cause correlations termed by chemists as complex formation or as association. Indeed, a wide range of degrees of association is observed in liquids and liquid mixtures and the concept of a molecule may require a careful definition. In favourable cases (12) itself may be used as a definition of the molecule, the result may be different from the usual concept adopted by chemists. In such a case the classification will be justified by the finding that correlated motions of the various spins

during an observation time of the order of 10^{-10} s yield a perfect prediction of $(1/T_1)_{\text{intra}}$.

However, in general one classifies the interactions due to the geometry of the ordinary chemical molecules. Nevertheless, the existence and the treatment of intermolecular correlations is a problem which makes the understanding and interpretation of intermolecular contributions to nuclear magnetic relaxation in liquids difficult and which has not been accorded proper attention in the literature in many cases.

Being concerned with intermolecular relaxation contributions one is usually faced with the magnetic dipole-dipole interaction as the relaxation mechanism. Indeed, in the present chapter only this interaction will be considered as the relaxation producing mechanism. Relaxation by spin-rotation and chemical shift anisotropy are usually considered typically intramolecular processes. This is true if the relaxing nucleus is part of a molecule. However, it has been shown recently that if the relaxing nucleus is located in a monoatomic ion, intermolecular spin-rotation and chemical shift anisotropy may determine $1/T_1$ (Schwartz 1976). There is also some evidence for such contributions to the relaxation of OH protons in the first hydration sphere of ions (Langer and Hertz 1977; Gill *et al* 1976).

If the relaxing nucleus possesses spin $I > 1/2$ the relaxation process is usually dominated by quadrupolar interaction. Also in this case $1/T_1$ may be governed by intermolecular interactions, if the nucleus is located within a monoatomic ion or an ion exhibiting spherical symmetry around the nucleus (Hertz 1973a, b; Weingärtner and Hertz 1977). For the latter topics the reader is referred to review articles recently published by various authors (Lindman and Forsén 1976, 1978; Wehrli 1979).

2.2 Some basic equations

According to the basic theory, the intermolecular relaxation rate $(1/T_1)_{\text{inter}}$ (as also the intramolecular one) is given by a linear combination of a number of spectral densities $J(\omega)$ (Abragam 1961; Hertz 1973b)

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = K \sum_i J(\omega_i). \quad (13)$$

The summation is over a set of frequencies ω_i given by the theory and K is a constant involving the nuclear properties of the interacting system. The frequencies ω_i are certain linear combinations of the nuclear magnetic resonance frequencies of the interacting nuclei. Let us treat here systems consisting of like spins I , the extension to systems of unlike spins being more complicated (Abragam 1961) details need not be considered, the final formulas to be used show only minor modifications. Then $(1/T_1)_{\text{inter}}$ is given by the relation

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \frac{8\pi}{5} \gamma_I^4 \hbar^2 I(I+1) \{ J(\omega) + 4J(2\omega) \}, \quad (14)$$

γ_I is the gyromagnetic ratio of the spin I , $J(\omega)$ is the Fourier transform of the time correlation function $G(t)$ describing the time evolution of the magnetic dipole-dipole interaction which was denoted by $V(r)$ in the introduction:

$$J(\omega) = \int_0^\infty G(t) \exp(-i\omega t) dt, \quad (15)$$

$$G(t) = \mathcal{N} \frac{\mathcal{Y}_2^{(0)}(\theta, \phi)}{r^3(0)} \cdot \frac{\mathcal{Y}_2^{(0)}(\theta, \phi)}{r^3(t)}, \quad (16)$$

$\mathcal{N}$ is the number of interaction partners. The vector $\mathbf{r}$ connects the reference nucleus with its interaction partner, $\mathbf{r}(0)$ is the vector at $t = 0$. The functions $\mathcal{Y}_2^{(m)}(\theta, \phi)$ are the spherical harmonics of second degree and m th order, depending on the polar and azimuthal angles θ and ϕ of the vector $\mathbf{r}$ relative to the laboratory system, the z -direction is defined by the magnetic field. The interaction partners undergo diffusion relative to each other, so we have $\mathbf{r} = \{\theta(t), \phi(t), r(t)\}$. Since in an isotropic system $G(t)$ does not depend on m (Hubbard 1969) the superscripts m may be dropped. Next, we reformulate (16) as first introduced by Oppenheim and Bloom and by Abragam (Oppenheim and Bloom 1961; Abragam 1961) to give

$$G(t) = \mathcal{N} \iint p(\mathbf{r}_0) \frac{Y_2(\theta, \phi)}{r^3} \frac{Y_2(\theta_0, \phi_0)}{r_0^3} P(\mathbf{r}_0, \mathbf{r}, t) d\mathbf{r}_0 d\mathbf{r}. \quad (17)$$

$4\pi r_0^2 p(\mathbf{r}_0) d\mathbf{r}_0$ is the probability of finding an interaction partner (spin I) within a spherical shell of volume $4\pi r_0^2 d\mathbf{r}_0$ around the reference nucleus selected at random. $p(\mathbf{r}_0)$ is the quantity we have already discussed, see (6). It will be seen that (15) and (17) together represent a verification of our statement that the expression (11) is of dominant importance to determine the intermolecular nuclear magnetic relaxation rate. A first coordination number with respect to the spin I may be defined *via* the area under the first peak of $p(\mathbf{r}_0)$

$$n_c = 4\pi \int_0^{r_1^*} p(r_0) r_0^2 dr_0, \quad (18)$$

where r_1^* defines the range of the first coordination sphere.

As already explained, the propagator $P(\mathbf{r}_0, \mathbf{r}, t)$ in (17) determines the probability that at time t a particle is in the volume element $d\mathbf{r}$ at $\mathbf{r}$ relative to the reference nucleus, if we know that it was at $\mathbf{r}_0$ at $t = 0$. Thus, the propagator involves the information on the dynamical behaviour of the system.

The fundamental importance of (17) for all further treatments requires some further comments. In (17) it has been assumed that the total correlation function is the sum of $\mathcal{N}$ independent correlation functions which implies that all cross terms between different particles are neglected. This results in the factor appearing before the integral in (17). To the authors' knowledge no treatment considering this and related problems of intermolecular nuclear magnetic interactions has been given as yet. However, it should be mentioned that other relaxation mechanisms, in particular quadrupolar interaction, are markedly influenced by such higher-particle correlations (Hertz 1973b).

Furthermore, it seems to be worth to recall the exact meaning of the propagator. By definition $P(\mathbf{r}_0, \mathbf{r}, t)$ yields the information on the motion of a particle *as seen from another one*, i.e. it is not the 'absolute' translational motion, measured in the laboratory system. Thus, in a strict sense $P(\mathbf{r}_0, \mathbf{r}, t)$ does not yield information on the self-diffusion process and $(1/T_1)_{\text{inter}}$ cannot be used to determine the self-diffusion coefficient D as recently suggested (Burnett and Harmon 1972). Rather, one has to introduce a model which relates self-diffusion to relative diffusion. This fact distinguishes the dynamic information obtainable from $(1/T_1)_{\text{inter}}$ from that available from quasielastic neutron scattering experiments and direct self-diffusion measurements. It is known from the theory of neutron scattering (Egelstaff 1967) that the intensity of the scattered neutrons

is the twofold Fourier transform of the translational propagator of the scattering particle, the latter being denoted as self-contribution of the van Hove correlation function. Therefore, within this nomenclature the propagator occurring in the theory of intermolecular dipole-dipole relaxation may be considered as a 'relative' self-contribution of the van Hove correlation function.

2.3 Model propagators and pair distribution functions

We see from (14), (15), and (17) that, in order to predict $(1/T_1)_{\text{inter}}$, we need the knowledge of both, the pair distribution function and the propagator. Thus the standard procedure would be to assume a certain $p(\mathbf{r}_0)$, to derive from this the propagator $P(\mathbf{r}_0, \mathbf{r}, t)$ by the aid of statistical mechanics and then to check by trial and error which $p(\mathbf{r}_0)$ gives the observed $(1/T_1)_{\text{inter}}$ as a function of the frequency ω and the temperature. Another possibility would be to choose a model pair distribution function which is characterized by a set of constant parameters, and likewise also to construct a model propagator which is described by a set of parameters. The experimental $(1/T_1)_{\text{inter}}(\omega)$ then may be used to determine all these parameters. Both these methods have not been applied yet. And more than this, with two exceptions to be discussed below (Hwang and Freed 1975; Pumpernik and Azman 1975) no attempts have been made to use coupled expressions for $p(\mathbf{r}_0)$ and $P(\mathbf{r}_0, \mathbf{r}, t)$. In view of this situation we have only to consider simple models depending on a small set of parameters either for the propagator or the pair distribution function. Then an approximation for $P(\mathbf{r}_0, \mathbf{r}, t)$ may be used to obtain information on $p(\mathbf{r}_0)$ and vice versa.

Before proceeding further we may ask: Do we in certain cases have knowledge of $p(\mathbf{r}_0)$ in molecular liquids with which nuclear spin relaxation data can be compared? In fact, an order of magnitude estimate is always given by simple density considerations. Apart from this at present experimental information is scarce. Certain information on $p(\mathbf{r}_0)$ may be obtained from scattering experiments (Zeidler 1980; Bertagnolli and Hertz 1978) but the particular interest in nuclear magnetic relaxation is devoted to proton distributions which are hard to obtain if isotopic substitution by deuterons is not feasible. Some progress has been obtained in a recent study on neutron scattering in the proton-carrying liquid CHCl_3 (Bertagnolli and Chieux 1980). Apart from such measurements further approximate information may be obtained by molecular dynamics simulations which have the advantage that beyond the equilibrium properties information on the dynamical behaviour are also provided (McDonald 1978; Kushik and Berne 1978).

2.3a. Models neglecting pair correlation effects: At first, we consider the propagator for the free diffusion. Assume that at $t = 0$ the nucleus is at $\mathbf{r} = 0$, then at a sufficiently long time we have (Abragam 1961)

$$P(\mathbf{r}_0, \mathbf{r}, t) = (4\pi Dt)^{-3/2} \exp(-r^2/4Dt), \quad (19)$$

which is the solution of the translational diffusion equation,

$$\frac{\partial P(\mathbf{r}, t)}{\partial t} = D \nabla^2 P(\mathbf{r}, t). \quad (20)$$

This Gaussian form of the propagator represents the long time limit in which all

choice is to convert the propagator in (19) to a relative one by replacing D by $2D$ as e.g. suggested by Oppenheim and Bloom (1961). This procedure implies that the translational motion of the particles is totally uncorrelated. Likewise, one may define a relative diffusion coefficient for liquid mixtures of unlike species A, B by $D_{\text{rel}} = 2\bar{D} = D_A + D_B$. In fact, from these arguments one sees that we have already the relative propagator in (9). As the simplest 'model' situation one may assume a random particle distribution up to a closest distance of approach a . Then $p(r_0)$ is given by the step function

$$p(r_0) = \begin{cases} 0 & \text{for } r < a \\ c' & \text{for } r \geq a \end{cases} \quad (21)$$

where c' is the number density of particles and a is the distance of closest approach between two spins. A distribution according to (21) has been termed as 'force free model' (Hwang and Freed 1975). The distribution of (21) is shown in figure 2 together with two other very simple model distribution functions. Introduction of these functions into (15) and (17) yields the relations first derived by Pfeifer (1961):

$$J(\omega) = \frac{v}{D} f(x) \quad (22)$$

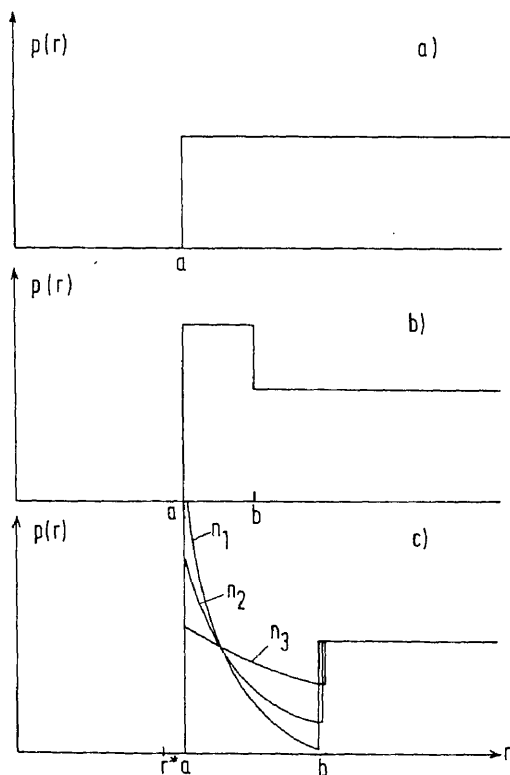


Figure 2. Three different possibilities to construct model atomic pair distribution functions.

Type (c) depends on the steepness parameter n , here we have $n_1 > n_2 > n_3$.

with

$$f(x) = \frac{2}{x^5} \left[\frac{x^2}{2} - 1 + \exp(-x) \left(\left(\frac{x^2}{2} - 1 \right) \sin x + \left(\frac{x^2}{2} + 2x - 1 \right) \cos x \right) \right]$$

and

$$x = \left(\frac{a^2 \omega}{D} \right)^{1/2},$$

where v takes account of the fact that the interaction partner may carry v spins.

Introduction of (22) in (14) allows an examination whether the propagator (19) is in principle correct by the observation of $(1/T_1)_{\text{inter}}(\omega)$. It should be recalled that in any case (22) involves the approximation (21).

At this point we should briefly consider the experimental situation. Due to the unavailability of sufficiently high magnetic fields the resonance frequencies $\nu_I = \omega/2\pi$ are limited to the order of some 100 MHz at the maximum for protons. However, for liquids of not very high viscosity *i.e.* diffusion constants in the order of some $10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, the characteristic time constants τ_c describing the decay of $G(t)$ may be estimated by the relation $\tau_c \approx a^2/3D$ (Hertz 1974), which are in the order of 10^{-11} sec . Thus we have $\omega\tau_c \ll 1$, this situation is termed the 'extreme narrowing' limit (Abragam 1961), now $1/T_1$ measures only the zero-frequency behaviour of $G(t)$, *i.e.*

$$J(\omega) = J(0),$$

and the frequency dependence of $1/T_1(\omega)$ cannot be realized experimentally. One way out of this difficulty would be to work at much lower temperatures. Unfortunately for most liquids the transition to the solid phase precludes this possibility. Consequently the method to investigate $P(\mathbf{r}_0, \mathbf{r}, t)$ is confined to those liquids (with molecules of moderate size) which can be cooled down sufficiently. Glycerol is a favourable example. In figure 3 we present the intermolecular proton relaxation rate as a function of I at two temperatures (Kintzinger and Zeidler 1973). The data have been fitted to (22) and partly to (26) to be given below. The resulting parameters are $a = 2.5 \cdot 10^{-8} \text{ cm}$, $\alpha = 0$ (see below) for $T = 30^\circ\text{C}$ ($D = 3.2 \cdot 10^{-18} \text{ cm}^2 \text{ sec}^{-1}$) and $a = 2.3 \cdot 10^{-8} \text{ cm}$, $\alpha = 0.003$ (see below) at $T = 13^\circ\text{C}$ ($D = 6.5 \cdot 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$). The diffusion coefficients have been measured independently (Tomlinson 1972; Preissing *et al* 1971). It may be seen from the figure that the quantitative fit is relatively poor, but qualitative agreement between theory and experiment is attained. There are fast processes which are not taken into account by (22).

In solutions containing paramagnetic particles the resonance frequency ω_s of the electron spin acting as the interaction partner is about three orders of magnitude larger than in those systems where the interaction partner is a nuclear spin. Thus, even with liquids of normal fluidity we have $\tau_c \omega_s \approx 1$. Now the form (13) which is valid for the relaxation caused by unequal spins has to be applied, details need not be given here. Studies with solutions of paramagnetic particles have the very great advantage that the intermolecular relaxation rate is the primary experimental quantity, no tedious isotopic substitution experiments are needed (see below). Moreover, the concentration of the electron paramagnetic interaction partner usually is relatively low which facilitates the consideration of relative and collective motions somewhat. Indeed, numerous experimental studies have been performed with solutions of free radicals (see *e.g.* Dally and Müller-Warmuth 1977, 1978, 1980; Nientied *et al* 1981), also the electron-nucleus

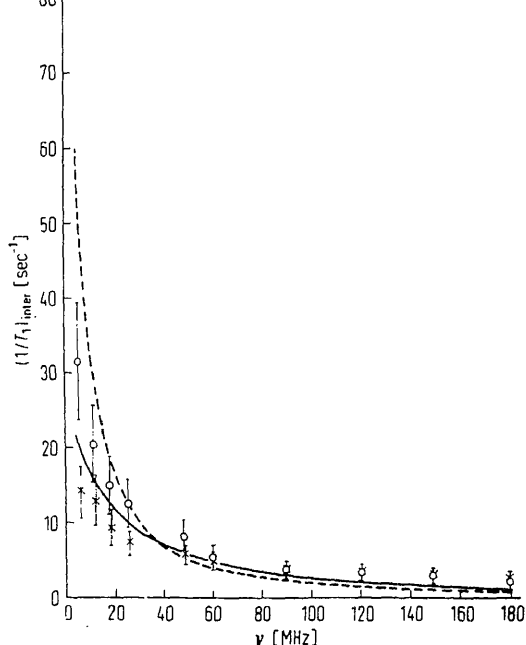


Figure 3. The intermolecular proton relaxation rate of glycerol as a function of the resonance frequency (Kintzinger and Zeidler 1973). $\times$: $1000/T = 3.3$; $\circ$: $1000/T = 3.5$. Dashed and solid lines: fits of the Torrey theory according to (26).

another technique to study the frequency dependence of the spectral density $J(\omega)$ as given by (15). It has been shown in these investigations that formulas of the type (13) give an approximate description of the experimental results. The order of magnitude of the self-diffusion coefficient which can be derived is correct, some typical deviations from the expected behaviour at high frequencies have been observed.

Before passing to the next type of approximation, we should mention a difficulty which is inherent in the reduction of the general distribution (4) to the atomic distribution function (6) and which indirectly was already mentioned. Apart from translational motions molecules may also perform rotational motions. Thus the short time behaviour of $P(\mathbf{r}_0, \mathbf{r}, t)$ may deviate from (19). The fluctuating dipolar interaction is only insensitive to such motion if the interacting nuclei reside in the centres of the molecules. Otherwise, the distance a does not refer to an interaction situation with spherical symmetry and furthermore, there may be an additional modulation of the spin-spin interaction due to molecular reorientation. Propagators which represent a superposition of rotational and translational movements have been given by Sears (1967) and Zeidler (1971). A correction of $(1/T_1)_{\text{inter}}$ by the 'off-center' effect has been discussed by Hubbard (1963). The correction factor is given by an expansion in even powers of s/r_s where s denotes the distance between the spin and the molecular centre and r_s denotes the effective radius of the molecular sphere. A typical situation with $s/r_s = 0.5$ yields an increase of $(1/T_1)_{\text{inter}}$ by 13 %. The theory has later been generalized by Harmon (1978) accounting for jump diffusion processes and Zeidler (1975) accounting for pair correlation effects.

parameter representation of $P(\mathbf{r}_1, t)$, and is based on the pioneering work of Torrey (1953). Torrey has considered the following model: A molecule is bound in a potential well for a mean time τ_i , after which it leaves the respective site and makes a jump and comes to rest in another well with displacement $\mathbf{r}_1$. After one jump the probability of finding a given displacement $\mathbf{r}_1$ is

$$P(\mathbf{r}_1) = (\frac{3}{2}\pi \langle r_1^2 \rangle)^{-1} \exp[-r_1/(\frac{1}{6}\langle r_1^2 \rangle)^{1/2}], \quad (23)$$

where $\langle r_1^2 \rangle$ is the mean square displacement caused by one jump. Defining the self-diffusion coefficient D by the relation

$$\langle r_1^2 \rangle = 6D\tau_i \quad (24)$$

and introducing a Poisson distribution of jumping times, the following expression for the propagator may be derived (Torrey 1953; Hertz 1974)

$$P(\mathbf{r}_0, \mathbf{r}, t) = (2\pi)^{-3} \int_0^\infty \exp\left[-2D\kappa^2 t/l + \frac{\langle r_1^2 \rangle}{\sigma} \kappa^2\right] \times \exp[-i\kappa(\mathbf{r} - \mathbf{r}_0)] d\kappa. \quad (25)$$

It will be seen that this propagator is characterized by the two parameters D and $\langle r_1^2 \rangle$. It is not an easy matter to state in which way this propagator is connected with the intermolecular interactions. The dependence of τ_i on E is of the type

$$\tau_i = \tau_i^0 \exp(E/kT),$$

where E is the effective potential depth, for the mean square path length $\langle r_1^2 \rangle$ no simple answer can be given. Insertion of (21) and (25) in (17) yields the intermolecular relaxation rate ($I = 1/2$, equal spins)

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \frac{3\pi}{5} \gamma^4 \hbar^2 \frac{c'}{a^3 \omega} \{f(\alpha, x) + 2f(\alpha, 2^{1/2}x)\} \quad (26)$$

with

$$f(\alpha, x) = \frac{2}{x^2} \left\{ v \left(1 - \frac{1}{u^2 + v^2} \right) + \exp(-2v) \left[v \left(1 + \frac{1}{u^2 + v^2} + 2 \right) \right] \right. \\ \left. \cos(2u) + \exp(-2v) u \left(1 - \frac{1}{u^2 + v^2} \right) \sin(2u) \right\}$$

and

$$u = \frac{1}{2} \left(\frac{q(1-q)}{\alpha} \right)^{1/2}; \quad v = \frac{1}{2} \left(\frac{q(1+q)}{\alpha} \right)^{1/2}; \quad q = \frac{\alpha x^2}{(1 + \alpha^2 x^4)^{1/2}}; \\ \alpha = \langle r_1^2 \rangle / 12a^2; \quad x = \left(\frac{\omega a^2}{D} \right)^{1/2}; \quad c' = N/V.$$

In the extreme narrowing situation, $\tau_i \omega \ll 1$, (26) simplifies to

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \pi \gamma^4 \hbar^2 \frac{c'}{a^3} \tau_i \left(1 + \frac{12}{5} \frac{a^2}{\langle r_1^2 \rangle} \right) \quad (27)$$

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \frac{8\pi}{9} \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \frac{c'}{a^3} \tau_i \left(1 + \frac{12a^2}{5\langle r_I^2 \rangle}\right) \quad (28)$$

h

$$\tau_i = \frac{\langle r_I^2 \rangle}{6D}$$

$$\bar{D} = \frac{1}{2}(D_I + D_S).$$

rey's relations have often been used to interpret $(1/T_1)_{\text{inter}}$. As an example we refer to the work of Kinzinger and Zeidler (1973). In connection with figure 3 we had already mentioned that a fitting procedure of the intermolecular relaxation rate to (26) added $\alpha = 0.003$, thus the mean flight length characterizing a hypothetical jump has been found to be much smaller than the closest distance of approach. In such a situation, $a^2/\langle r_I^2 \rangle \gg 1$, (27) and (28) pass to the relations

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \frac{2}{3} \pi \gamma^4 \hbar^2 \frac{c'}{aD}; \quad I = \frac{1}{2} \quad (29)$$

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \frac{8}{15} \pi \gamma^4 \hbar^2 I(I+1) \frac{c'}{aD}; \quad (\text{for any } I) \quad (29a)$$

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \frac{16}{45} \pi \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \frac{c'}{a\bar{D}}. \quad (30)$$

is clear that in the situation of extreme narrowing D and τ_i cannot be determined separately. A general procedure is to determine D by independent self-diffusion measurements and then to calculate τ_i . However, even in the 'non-extreme narrowing' situation where the frequency dependence of $(1/T_1)_{\text{inter}}$ may be measured one should be cautious in determining dynamical details by this method. This can only be done if the effective observation time $\tau_{\text{obs}} = (\mathcal{H}^2 D)^{-1}$ is smaller than the time constants describing the various elementary processes (Hertz 1974). Therefore, we have to find the smallest value of τ_{obs} which enters into $(1/T_1)_{\text{inter}}$. $G(t)$ has essentially decayed when the spherical harmonics have changed their sign. The smallest displacement which may cause such a behaviour is of the order of a and the corresponding observation time is of the order $\tau_{\text{obs}} \approx a^2/D$ (Hertz 1974). Rewriting the exponential in (25) in a suitable form yields the result

$$\exp\left[-2t/\left(\tau_{\text{obs}} + \frac{\langle r_I^2 \rangle}{6D}\right)\right],$$

which means that $\langle r_I^2 \rangle$ or τ_i can be observed only if $\langle r_I^2 \rangle \gg a^2$. Whereas jump diffusion models for liquids have been under debate for a long time, it seems now to be accepted that mean square (free path) jump lengths of the order of molecular diameters do not occur, rather translational motions in liquids are well described by continuous micro-step diffusion processes (Rahman and Stillinger 1971; Stillinger and Rahman 1974). Thus, the omission of jump diffusion does not seem to be the reason for the deficiency of (22), though inclusion of such effects may bring the theoretical prediction closer to the experimental findings.

2.3b Models taking into account pair correlation effects: We must expect that an important reason for the shortcoming of the above theories is the neglect of pair correlation effects. In fact, the intermolecular interactions in molecular liquids do cause deviations from random particle distribution leading to pair distribution functions of a general type as shown in figure 1. Already in 1957 it had been pointed out that a correct theory should include realistic models for $p(\mathbf{r}_0)$ (Seiden 1957). So various authors have introduced simple model distribution functions and then connected them with a continuous diffusion or Torrey's model to describe the motional part (Harmon and Muller 1969; Krynicky 1966; Oppenheim and Bloom 1961; Göller *et al* 1972). However $(1/T_1)_{\text{inter}}$ has turned out to be not very sensitive to weak maxima in $p(\mathbf{r}_0)$.

Considering the range of possible variation of $p(\mathbf{r}_0)$, the models discussed in §2.3a must be taken as a particular limiting case, *i.e.* we were concerned with systems of weak intermolecular interaction, as already mentioned above. Another limiting case is obtained if the intermolecular potential between the interaction partners has a deep minimum such that there is a tight binding between the molecules. In this case the intermolecular distances between the molecules will remain unchanged during the observation time of $\approx 10^{-11}$ sec. Then $p(\mathbf{r}_0)$ can be approximated by a δ -function and $P(\mathbf{r}_0, \mathbf{r}, t)$ degenerates to a rotational propagator (Abragam 1961; Hertz 1973c)

$$P(\mathbf{r}_0, \mathbf{r}, t) = \sum_{l, m} Y_l^{m*}(\theta_0, \phi_0) Y_l^m(\theta, \phi) \exp[-l(l+1)D_r t], \quad (31)$$

where D_r is the rotational diffusion coefficient of the molecular system consisting of the associated particles. The rigorous application of this concept leads to the relations for intramolecular relaxation rates as derived by Abragam (1961). The application of (31) to systems with intermolecular binding will be given below.

Clearly, any real system lies between these two limiting cases. Thus, in principle a rotational contribution as given in (31) should in some way be combined with the translational propagator according to (19) or (25). Such a procedure has indeed been performed for electrolyte solutions in various versions (Kramer *et al* 1965; Hertz 1967c).

Up to now we only have considered the attractive part of the intermolecular potential to be the reason demanding the incorporation of configurational and notional correlations in the treatment. But even if the attractive forces are weak, there remains the repulsive part of the potential which has its simplest manifestation in the volume of the reference molecule not being accessible for the interaction partners. Moreover, if $\bar{n}$ molecules have given positions, one is not entirely free to choose the position of the $\bar{n} + 1$ 'th molecule. Thus, rigorously the N spin-spin magnetic interaction pairs are not independent of one another. The corresponding contribution, termed as excluded volume effect, has been a long standing problem. Only recently two groups of workers have independently analyzed this effect. The idea of Hwang and Freed (1975) is to superimpose on the free diffusion a current directed such that the particles are driven away from the interaction partners. This desired property is obtained by deriving the propagator from the Smoluchowski equation which may be considered as a generalization of Fick's law defining the propagator in (20):

$$\frac{\partial P(\mathbf{r}_0, \mathbf{r}, t)}{\partial t} = D_{\text{rel}} \nabla \left(\nabla P(\mathbf{r}_0, \mathbf{r}, t) + \frac{1}{kT} P(\mathbf{r}_0, \mathbf{r}, t) \nabla \tilde{E}(\mathbf{r}) \right) \quad (32)$$

clearly (32) passes into the free diffusion limit if the second term on the right-hand side of (32) becomes negligible, then at $t > 0$ the Gaussian form of the propagator is obtained. However, in general, on the free diffusion the current

$$-D_{\text{rel}} \cdot \frac{1}{kT} P(\mathbf{r}_0, \mathbf{r}, t) \nabla \tilde{E}(\mathbf{r})$$

superimposed which drives the particles away from each other.

The potential of mean force $\tilde{E}(\mathbf{r})$ is already well known to us, it is related to the pair distribution function as given in (6). Three subcases have been treated. Only if $p(\mathbf{r}_0)$ is given by (11)—‘force-free-model’—an analytical solution is possible. We are mainly interested in the extreme narrowing limit, then one obtains

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \frac{16\pi}{27} \gamma^4 \hbar^2 I(I+1) \frac{c'}{aD} = 1.11 \left(\frac{1}{T_1}\right)_{\text{inter}}^{\text{AT}} \quad (33)$$

where $(1/T_1)_{\text{inter}}^{\text{AT}}$ stands for the Abragam-Torrey limit, (29a). In this case the effect of the excluded volume does not influence $(1/T_1)_{\text{inter}}$ very drastically. The two other pair correlation functions considered by the authors are the hard sphere pair correlation function based on the Percus-Yevick equation (Egelstaff 1967) and a hard sphere pair correlation function obtained from computer simulation, but in these cases the numerical efforts to get the solution are considerable.

At the same time Ayant *et al* (1975) have solved the translational diffusion equation subject to the boundary condition at the surface of a hard sphere. This treatment corresponds totally to the ‘force-free model’ discussed above and the results in both papers are identical.

Summarizing at this stage we feel that the improvements of the Abragam-Torrey theory on a more rigorous level, though of considerable interest for the understanding of the underlying physical processes, do not yield a substantial improvement of agreement between experimental results and theoretical predictions. Moreover in some cases the computational efforts to be made are considerable. On the other side, as a positive result of the many investigations dedicated to the intermolecular relaxation rate as such—including temperature and frequency dependences—we should state that it has been confirmed that the self-diffusion coefficient of the molecules carrying the relaxing spins essentially gives the correct description of the motional processes entering in the total mechanism of nuclear magnetic relaxation.

4 The simple approach for $(1/T_1)_{\text{inter}}$ used in the Karlsruhe laboratory

All treatments so far mentioned turned out to be mathematically difficult because of the particular functional dependence of the propagator on $\mathbf{r}_0$ and $\mathbf{r}$. This is still the case if we only treat the limiting case of extreme narrowing $\omega\tau \ll 1$, which as we had explained, has the greatest practical importance due to the high fluidity of ordinary liquids. So, all the formulas to be given in this section only refer to the situation of extreme narrowing. In order to simplify the computation we may say that the decay of the correlation function is caused primarily by the rotation of the vector connecting the reference

These arguments lead us to the use of the rotational propagator (31) made in (17). Then, after integration over all orientations we obtain from (17)

$$G(t) = 4\pi \exp(-t/\tau_c^*) \int_0^\alpha p(r_0) r_0^2 dr_0 / r_0^6, \quad (34)$$

where τ_c^* is the correlation time which governs the decay of $G(t)$ and which now we have to consider. The time after which a partner molecule has moved from one side of the reference molecule to the other is

$$\tau_r \approx (2r_m)^2 / 2 \cdot 2\bar{D} = r_m^2 / \bar{D},$$

r_m = separation between the centre of masses of the reference and partner molecule. In order to take account of the relative motion we have taken $2\bar{D}$. We are interested in the correlation time of the spherical harmonics of second order, thus

$$\tau_m = r_m^2 / 3\bar{D}.$$

Taking also into account the tumbling of the molecules and the fluctuation of the distance between the molecules one arrives at the estimate (Hertz 1974)

$$\tau_c^* = a^2 / 3\bar{D}, \quad (35)$$

where, as before, a is the closest distance of approach between the two interacting nuclei.

Now any radial distribution function may be introduced in (34). Let us choose the two functions shown in figure 2. The distribution function c may be written as

$$\begin{aligned} p(r_0) &= \frac{p_0}{(r_0 - r^*)^n} \quad \text{for } a \leq r_0 \leq b, \\ p(r_0) &= c' \quad \text{for } r_0 > b, \end{aligned} \quad (36)$$

as before c' is the spin concentration in the bulk liquid, p_0 is given by the relation

$$4\pi \int_a^b p(r_0) r_0^2 dr_0 = n_c$$

where n_c is the first coordination number around the molecular group carrying the reference nucleus. For the parameters r^* and b we set:

$$\begin{aligned} r^* &= ka \\ b &= la \end{aligned}$$

we set $k = 0.9$.

With this distribution function and with (34), (17), (15) and (14) ($\omega = 0$) one obtains the intermolecular relaxation rate (like spins, $I = 1/2$) (Hertz and Rädle 1973)

$$\left(\frac{1}{T_1} \right)_{\text{inter}} = \frac{1}{2} \gamma^4 \hbar^2 \frac{n_c}{a^4 \bar{D}} g(n, k, l) + \delta^*, \quad (37)$$

where the function $g(n, k, l)$ is depicted in figure 4. On the other hand, with the distribution function b of figure 2 the result is

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \frac{1}{2} \gamma^4 \hbar^2 \frac{n_c}{a^4 D} + \delta^*,$$

in both cases

$$\delta^* = \frac{2\pi}{3} \gamma^4 \hbar^2 \frac{c'}{bD}. \quad (38)$$

Equation (37) contains three parameters: the steepness of the pair distribution function, *ie* the depth of the attractive potential, characterized by n , the first coordination number n_c of the group or molecule containing the relaxing nucleus, and b , the radius of the second coordination sphere. It may be shown that satisfactory agreement between experimental results and (39) can be achieved if the experimental diffusion coefficients are used and if the parameters n , n_c and b are suitably chosen, see table 1.

It will be seen that (38) is just the Abragam-Torrey limiting formula given as (29), the only difference is that now the numerical factor $3/5$ is replaced by the factor $2/3$, which is an improvement. In fact, whereas the Torrey formula usually yields closest distances a which are too small, (35), when applied alone, leads to more reasonable values of the closest distance of approach. As will be demonstrated with a number of examples below, for a wide range of common organic liquids closest distances of approach $a = 2.5 - 4 \text{ \AA}$ are obtained with (37).

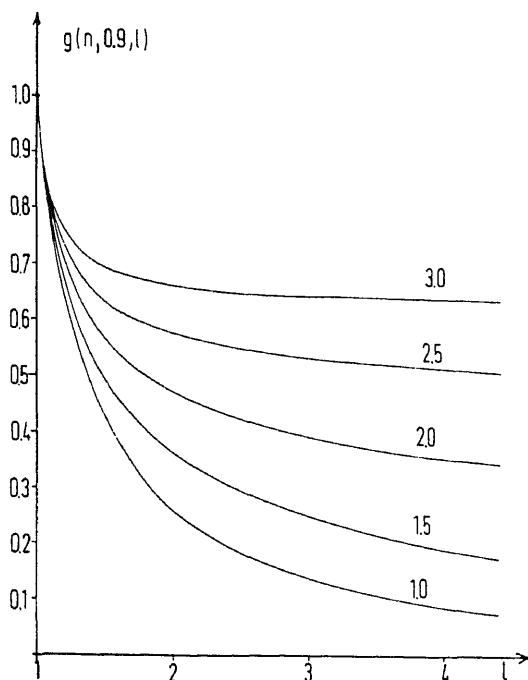


Figure 4. The quantity $g(n, k, l)$, characterizing the mean value of $1/r^6$, as a function of the geometry parameter l (see text). The parameter at the various curves is the steepness parameter

Table 1. Methyl halides: intermolecular relaxation rates, closest distances of approach between protons, potential steepness parameter n , and some other structural and dynamic data.

Compound	$(1/T_1)_{\text{inter}}$ at 25°C (S ⁻¹)	$a(\text{\AA})$	$b(\text{\AA})$	n	$(2r)_{\text{M}} (\text{\AA})^{\text{iv}}$	D (10 ⁻⁵ cm ² sec ⁻¹)	E_A (kJ/mol)	References ^v
CHCl ₃	9.3×10^{-3}	4.1	8	1.2	5.76	2.5		Caparelli <i>et al</i> (1976); Bender and Zeidler (1971)
CFCl ₃	4.0×10^{-3} i	4.5	10	1.0	6.04	2.65	9.08	Gillen and Griffith (1972)
CBrCl ₃	1.75×10^{-2}	4.5	10	1.7	6.12	0.8 ⁱⁱ	12.4	Huang and Rogers (1978)
CH ₂ Cl ₂	1.0×10^{-2}	4.5	10	1.3	5.26	3.85	7.82	Sandhu (1978);
CH ₂ Br ₂	1.8×10^{-2}	4.5	12	1.2	5.54	1.55	9.12	Sandhu (1977); Sandhu (1969)
CH ₂ I ₂	4.4×10^{-2}	4.5	12	1.2	5.76	0.56	13.1	Sandhu and Peemoeller (1976); Sandhu (1969)
CH ₃ Br	1.1×10^{-2}	4.5	12	1.6	5.12	3.6 ⁱⁱⁱ	9.62	Lassigne and Wells (1977b)
CH ₃ I	1.6×10^{-2}	4.5	10	1.3	5.32	3.5	10.0	Gillen <i>et al</i> (1971); Zeidler (1965)

i) Extrapolated from low temperature data; ii) estimated from viscosity data; iii) self-diffusion coefficient of C₇H₅Br (McLaughlin 1959); iv) molecular diameter as estimated from molar volume V_M , filling factor 0.666; v) if two references are given then the second one refers to self-diffusion coefficients; the first coordination number with respect to the molecule has been taken to be $n_c = 4$ in all cases.

3. Experimental results for pure liquids

3.1 Some general aspects

In a pure liquid a rigorous separation of $(1/T_1)_{\text{inter}}$ from intramolecular contributions is only possible on performing isotopic substitution experiments (Bonera and Rigamonti 1965; Zeidler 1965). With this method one uses the fact that there may exist more than one isotope of an element exhibiting different gyromagnetic ratios. Such a procedure cannot be performed for all nuclei, but fortunately the isotope pair proton-deuteron allows such measurements.

On the other hand, in a number of liquids showing hydrogen bond formation the isotopic substitution method cannot be applied to the H-bond protons. This is a consequence of the delocalization of the respective proton which we have described in connection with the definition of the H-bond in §1. A method to suppress the exchange effect and to determine $(1/T_1)_{\text{inter}}$ in favourable cases for H-bond protons as well (Goldammer and Zeidler 1969) has been reported. In the other systems in which proton relaxation is to be observed, and for the alkyl protons of H-bonded liquids, one has to measure $1/T_1$ in a mixture of the normal molecule (containing a OD group for H-bonded liquids) with the fully deuterated molecule. Denoting the mole fraction of the proton containing species by x_H , we have

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)_{\text{intra}} + \left(\frac{1}{T_1}\right)_{\text{inter}} [x_H + \varepsilon(1 - x_H)] \quad (39)$$

$$\varepsilon = \frac{\frac{2}{3} \gamma_D^2 I_D (I_D + 1)}{\gamma_H^2 I_H (I_H + 1)} = 0.042.$$

Thus measurements at (at least two) different proton concentrations allow a separation of both contributions. Strictly (39) is only valid if both the normal and the deuterated liquid have the same viscosity, otherwise the difference must be taken into account by an appropriate correction.

Let us briefly discuss the various possibilities for application of (39). If the reference molecule carries more than one proton the intermolecular relaxation rate is usually less than 50% of the total contribution. On the other hand, the molecule often carries no equivalent magnetic nucleus apart from the reference one and the intramolecular contribution with respect to the partial nuclear magnetization considered vanishes. Thus $1/T_1$ directly reflects $(1/T_1)_{\text{inter}}$. Examples are the relaxation of OH protons in alkyl deuterated alcohols (Güner and Hertz 1972; Bender and Hertz 1977; Berg *et al* 1976), acids, or of formyl protons in HCOOD (Kratochwill and Hertz 1977) and HCOOND₂ (Leiter *et al* 1983). A reduction of $(1/T_1)_{\text{intra}}$ has also been achieved using partially deuterated methyl groups in the compounds CD₂HOD (Gill *et al* 1976), CD₂HCN (Tokuhira 1979), and CD₂HCD₂COOH (Hertz and Radle 1973).

However, often mechanisms other than dipolar, and in particular spin rotation interaction, cannot be neglected. Thus the proton in CHCl₃ relaxes by intermolecular dipole-dipole and spin rotation interaction (Bender and Zeidler 1971). Since both contributions differ in the sign of the temperature dependence suitable measurements have been performed to separate the two mechanisms (Dinesh and Rodgers 1972). Regrettably, the respective results of Dinesh and Rodgers deviate remarkably from the results of the dipole-dipole interaction measurements (Dinesh and Zeidler 1972).

intermolecular contributions. Instead of diluting in the deuterated analogue one may dilute the proton carrying species in a magnetically inert solvent such as CCl_4 . However, in the latter case one is concerned with the problem that the correlation time describing the motion of the dissolved molecule differs from that in the pure state. Likewise, one may estimate $(1/T_1)_{\text{intra}}$ *via* the deuteron relaxation rate. These procedures are of importance in those cases where proton exchange between the molecules does not allow the separation of $(1/T_1)_{\text{inter}}$ *via* the usual isotopic dilution experiment.

3.2 Proton-proton distributions

The earlier work on (inter) molecular relaxation in liquids has been summarized by one of the present authors (Hertz 1967a). To the authors' knowledge no further review including intermolecular relaxation in liquids has been published since then. Most of the earlier data have been reported by Zeidler (1965) who performed the first systematic investigations using the isotopic substitution technique. It should be mentioned that meanwhile T_1 for some systems have been reported which are slightly longer than the values obtained by Zeidler (1965). In this situation one is justified in assuming that the longer T_1 results are the better ones since impure substances and unsuitable equipment have the tendency to shorten T_1 values. The pertinent results of these studies in the light of intermolecular forces will be discussed below.

The following considerations refer only to such work where $(1/T_1)_{\text{inter}}$ has been determined *via* the isotopic dilution experiment. Only in cases where such an experiment is not possible other methods are considered. There are numerous papers where intra- and intermolecular contributions have been determined by alternative methods or by an estimate of $(1/T_1)_{\text{intra}}$. Clearly, such methods cannot give substantial results on intermolecular relaxation rates.

3.2a Hydrocarbons: Only a small amount of work has been done. Harmon and Muller (1969) have studied the intermolecular proton relaxation rate in liquid ethane. Their conclusion that diffusion occurs *via* a jump process has recently been criticized by Hwang and Freed (1975) who have pointed out that the failure of the theoretical approach of the Torrey theory may be a consequence of other sources, in particular the 'excluded volume effect'. Data on proton relaxation in cyclohexane and benzene have been summarized by Zeidler (1965).

3.2b Methyl halides: This class of compounds may serve as model or representative compounds for small molecules without strongly specific interactions and without internal flexibility. Within this context there have been a large number of investigations on the dynamical behaviour of such molecules. However, though a lot of data on $(1/T_1)_{\text{inter}}$ may be found in the respective papers the authors' main interest has been devoted to the intramolecular contributions.

A survey on the respective data on $(1/T_1)_{\text{inter}}$ is given in table 1. In the second column the intermolecular relaxation rate is shown. Since the values at 298 K are partly taken from graphical representations or are interpolated from the original data, they may involve certain errors. The seventh column shows the corresponding self-diffusion coefficients.

contains only one proton and the deviation from spherical shape is still tolerable. At 298 K we have $(1/T_1)_{\text{inter}} = 9.3 \cdot 10^{-3} \text{ sec}^{-1}$, the self-diffusion coefficient is about $2.5 \cdot 10^{-5} \text{ cm}^2/\text{sec}$ (Bender and Zeidler 1971). The Abragam-Torrey formula (29) yields a distance of closest approach between the protons of $a = 2.6 \text{ \AA}$. Models show that this value is far too small, i.e. the interaction constant works out to be too small. The Hubbard correction (Hubbard 1963) yields a variation of about 10% of the $(1/T_1)_{\text{inter}}$ value calculated from the Abragam-Torrey formula. Also the application of the relation by Hwang and Freed, accounting for the 'excluded volume' effect, yields no substantial improvement.

Let us consider the model evaluated by one of the present authors (HGH), see (37) and (38). For liquids without strong specific interactions the intermolecular potential is flat. In these cases $g(n, k, l) \approx 0.3$ has proved to be a reasonable value. With $b = 8 \text{ \AA}$ the translational contribution due to the protons beyond the first coordination sphere yields $(1/T_1)_{\text{inter}}^{\text{II}} = 4.5 \cdot 10^{-3} \text{ sec}^{-1} = \delta^*$. With $n = 1, 2$ and a first coordination number $n_c = 4$ one derives from (37) and (38), $a = 4.1 \text{ \AA}$. From the density of the liquid one estimates a diameter of the chloroform molecule, $d \approx 5.8 \text{ \AA}$. Recent neutron scattering experiments on chloroform have yielded a first peak in the proton distribution at about $4.3 \text{ \AA}$ which is also in good agreement with the above result (Bertagnolli 1981). Equations (37) and (38) have also been used for the evaluation of the closest distances of approach for other methyl halides collected in table 1.

For compounds of type MeX_2H_2 the difficulty is that there are two protons in equal positions. This may cause a splitting of the first peak in the proton distribution. In principle one may account for this situation choosing a model pair distribution function which exhibits two peaks. However, since the protons are chemically equal it seems to be more appropriate to calculate an effective distance assuming a coordination number, vn_c , where v is the number of equivalent protons and n_c is the first coordination number with respect to the molecules. Then the effective distance is an appropriate mean value; one should recall that it is not the algebraic mean, rather a $1/r^6$ weighted value according to the particular form of (37) when it is rewritten in the form

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \frac{1}{2} \gamma^4 \hbar^2 g(n, k, l) \frac{vn_c}{a^6} \tau_c^* + \delta^*.$$

It will be seen from the data summarized in table 1 that the figures obtained are physically reasonable. In particular, the potential steepness parameter n is close to unity in all cases which demonstrates that the intermolecular forces between these molecules are weak. Strictly speaking, our information refers to the H-H part of the intermolecular potential.

3.2c Nitriles: Proton intermolecular relaxation rates were determined by Zeidler (1965) at 25°C and by Woessner *et al* (1969) in the temperature range -40 to 70°C . ^{13}C - ^1H intermolecular relaxation rates of the nitrile carbon were evaluated by Leipert *et al* (1974) using an indirect procedure—experimentally separating the non-dipolar part with the help of double resonance techniques and subtracting the calculated intramolecular contribution from the dipolar relaxation rate. A direct method was used by Kratochwill (1978) measuring ^{13}C relaxation rates in system $\text{CD}_3\text{-}^{13}\text{CN/CH}_3\text{CN}$. By combining ^1H - ^1H and ^{13}C - ^1H intermolecular dipolar relaxation rates and the self-

x-ray investigation of liquid acetonitrile (Kratochwill *et al* 1973). Using the model atomic pair distribution functions inherent in the detailed 'correlation cluster model' of the x-ray investigation intermolecular relaxation rates were calculated, which were in good agreement with the experimental values, *eg* at 25°C: $1/T_1(^1\text{H}-^1\text{H}) = 1.88 \cdot 10^{-2} \text{ sec}^{-1}$ (expt: $1.80 \cdot 10^{-2} \text{ sec}^{-1}$; Zeidler 1965) and $1/T_1(^{13}\text{C}-^1\text{H}) = 1.12 \cdot 10^{-3} \text{ sec}^{-1}$ (expt: $1.05 \cdot 10^{-3} \text{ sec}^{-1}$; Kratochwill 1978).

4. The detection of association by the study of the A parameter

4.1 Association between equal molecules

The knowledge of the intermolecular relaxation rate can be used to detect molecular association in liquid mixtures, the term association being understood as a configurationally well defined concept. We are confining the treatment here to binary mixtures; let us denote the two components as 1 and 2. We first consider a possible association between particles of similar kind and begin with the definition of the first coordination number of atom i with respect to such atoms i which are not members of the same molecule. We note that the concept of a first coordination number never refers to a sharply defined quantity, so we shall give here a number of possible definitions which are more or less equivalent. This conceptual development will facilitate the understanding of the more general definition to be presented. We begin with the most conventional form which we have already used in (18) and (37). The first intermolecular coordination number of atom i with respect to another atom i is given by the expression

$$\begin{aligned} n_{ii} &= 4\pi \int_0^{r_i^*} p_{ii}(r) r^2 dr \quad i = 1, 2 \\ &= 4\pi c'_i \int_0^{r_i^*} g_{ii}(r) r^2 dr, \end{aligned} \quad (40)$$

where r_i^* is the location of the first minimum of $g_{ii}(r)$ (see figure 1), and g_{ii} is the atomic pair correlation function of species i . c'_i is the corresponding number density. Thus we have

$$p_{ii}(r) = c'_i g_{ii}(r). \quad (41)$$

Now we rewrite (40) in the form

$$n_{ii} = 4\pi c'_i \int_0^{\alpha} \delta_{ii}(r) g_{ii}(r) r^2 dr, \quad (42)$$

where δ_{ii} is a step function having the property

$$\begin{aligned} \delta_{ii}(r) &= 1 \quad \text{for } 0 < r \leq r_i^*, \\ \text{and} \quad \delta_{ii}(r) &= 0 \quad \text{for } r > r_i^*. \end{aligned} \quad (43)$$

Next we modify the function $\delta(r)$ so that it is represented by a Gaussian function,

$$\delta'_{ii}(r) = \exp[-\alpha(r-a)^2], \quad r \geq a. \quad (44)$$

According to this defining function we have a modified kind of a first coordination number,

$$n_{ii}' = 4\pi c_i' \int_a^\infty \delta_{ii}'(r) g_{ii}(r) r^2 dr, \quad (45)$$

where a is a certain atom-atom distance which we may again call the closest distance of approach. The constant α characterizes the width of the region we wish to count as belonging to the first coordination sphere. At $r' = a + (1/\alpha)^{1/2}$ we have $\delta_{ii}'(r) = e^{-1}$, thus r' should be $\approx r_1^*$.

Finally, we may also define the first coordination sphere by the function

$$\delta_{ii}^* = a^6/r^6$$

so that we have

$$n_{ii}^* = 4\pi c_i' a^6 \int_a^\infty \delta_{ii}^*(r) g_{ii}(r) r^2 dr \quad (46)$$

$$= 4\pi c_i' a^6 \int_a^\infty \frac{g_{ii}(r)}{r^6} r^2 dr, \quad (47)$$

where now we have $\delta_{ii}^*(r) = 1/e$ for $r = ae^{1/6} = 1.16 a$.

The next step is to introduce reduced first coordination numbers $(n_{ii})_r$, $(n_{ii}')_r$, and $(n_{ii}^*)_r$ by the definitions

$$(n_{ii})_r = n_{ii}/c_i' \quad (40a)$$

$$(n_{ii}')_r = n_{ii}'/c_i' \quad (45a)$$

$$(n_{ii}^*)_r = n_{ii}^*/c_i'. \quad (47a)$$

It will be seen that in the event that $g_{ii}(r)$ is independent of the composition over the entire composition range, the reduced first coordination numbers are strictly constant quantities. Or, expressed in other words, in this situation the first coordination number of atom i with respect to i is proportional to the number density of i . Thus we say, if in a given mixture $g_{ii}(r)$ does not change with the composition, then there is no association in this system with respect to the atomic species i . If, however, with decreasing concentration of component i the corresponding reduced first coordination number $(n_{ii})_r$ increases, then we say that i - i intermolecular atomic association exists in the mixture. In terms of $g_{ii}(r)$ this means that $g_{ii}(r)$ changes its form such that the product $\delta_{ii}(r)g_{ii}(r)$ becomes larger, ie $g_{ii}(r)$ becomes larger in those regions where $\delta_{ii}(r)$ is larger and this is in the close neighbourhood of the reference atom. This way of systematic description requires a designation for a situation which usually is not employed. Namely, we may also have the case that the reduced first coordination number $(n_{ii})_r$ decreases if the concentration of i decreases. Now we say that on diluting the component i , de-association with respect to atom i occurs in the mixture. It is clear that in this event the pair correlation function $g_{ii}(r)$ changes its form such that in regions around the reference atom for which $\delta_{ii}(r)$ is already small $g_{ii}(r)$ increases whereas in the regions of direct contact $g_{ii}(r)$ becomes smaller.

The results which we have obtained by these arguments have now to be introduced in the expressions for the intermolecular relaxation rate as given by (14). First we insert

where, as we did before, we have used (35) as an estimate for the correlation time τ_c^* . If we divide (48) by c'_i/D and take into account (47a), we obtain

$$\left(\frac{1}{T_i}\right)_{\text{inter}} \cdot \frac{D}{c'_i} = \frac{1}{2} \gamma^4 \hbar^2 \frac{1}{a^4} (n_{ii}^*)_r \quad (49)$$

Now we denote the quantity on the left-hand side of (49) by A , the association parameter,

$$\left(\frac{1}{T_i}\right)_{\text{inter}} \cdot \frac{D}{c'_i} \equiv A \quad (50)$$

and applying the formulations given above, we can make the following statement: If we are justified in assuming that the closest distance of approach, a , is a constant quantity, then we have no association in the liquid mixture if A remains constant throughout the total composition range; there is association with respect to atom i if A increases with decreasing c'_i , and in the case of a decreasing A as c'_i becomes smaller, de-association with respect to atom i occurs.

We may also apply the A parameter in connection with (37). Then we have

$$A_{ii} = \left(\frac{1}{T_i}\right)_{\text{inter}} \cdot \frac{D}{c'_i} = \gamma^4 \hbar^2 \left[\frac{g(n, k, l)}{2a^4} (n_{ii})_r + \frac{2}{3} \frac{\pi}{b} \right], \quad (51)$$

where the definition (40a) for the reduced first coordination number has been used. With (51) an observed increase of A cannot exclusively be identified as indicating an increase of the reduced first coordination number, rather a part of the effect has also been assigned to the factor $g(n, k, l)$, so that apart from the additive constant term $2/3\pi b$, the product $g(n, k, l) \cdot (n_{ii})_r$ corresponds to the more general reduced first coordination number $(n_{ii}^*)_r$, occurring in (49). In principle it may be that also the closest distance of approach varies with decreasing concentration c'_i . Then it is quite natural also to interpret a decrease of a as a higher degree of association and vice versa. In fact, a decrease of the distance of approach a causes an increase of A , so that the statement that A is a tool to detect the occurrence of i - i association remains valid.

4.2 Some experimental results for equal particle association as identified through the A parameter

Before we quote some experimental results for the association parameter A , a general remark should be made concerning the experimental uncertainty. As was explained above, the intermolecular relaxation rate is the difference between the total relaxation rate and the intramolecular relaxation rate. As $c'_i \rightarrow 0$ the intermolecular relaxation rates vanishes, whereas the intramolecular relaxation rate remains a finite quantity. Thus one is confronted with the experimental problem of measuring a quantity which is the small difference between two comparatively large numbers. The experimental results so far available have been obtained from primary measurements with an experimental uncertainty of the total and intramolecular relaxation rate which is at best

moderate degree of dilution have a limit of error of $\pm 20\%$.

The most important type of intermolecular interaction where one would certainly expect an increase of A with an increasing degree of dilution of the interacting molecules is the H-bond formation. And indeed, the effect in question here has been observed for the system ethanol/ CCl_4 (Bender and Hertz 1977). Some data are depicted in figure 5. The increase of A is strongest for the OH group, however for the CH_2 and CH_3 protons as well H-H association is detectable. It is interesting to note that in the solvent water, ethanol-ethanol association could not be observed (Hertz and Tutsch 1976). Methanol in the mixture with benzene has also been studied (Ansari and Kratochwill 1978), the association of the OH hydrogen can clearly be seen, the A coefficient corresponding to the methyl hydrogen remains constant over the composition range. This is also the case for the methyl groups of methanol in the mixture with pyridine (Helm and Kratochwill 1978), however in this system the A coefficient for OH decreases with decreasing alcohol concentration, thus, as has been explained above, we observe a de-association of the OH hydrogen in the solvent pyridine.

Let us now turn to the carboxylic acids. Here the first investigations pertinent to our association criterion were performed on aqueous mixtures with butyric, propionic and acetic acids (Hertz and Tutsch 1976). In these systems again the arguments given in the

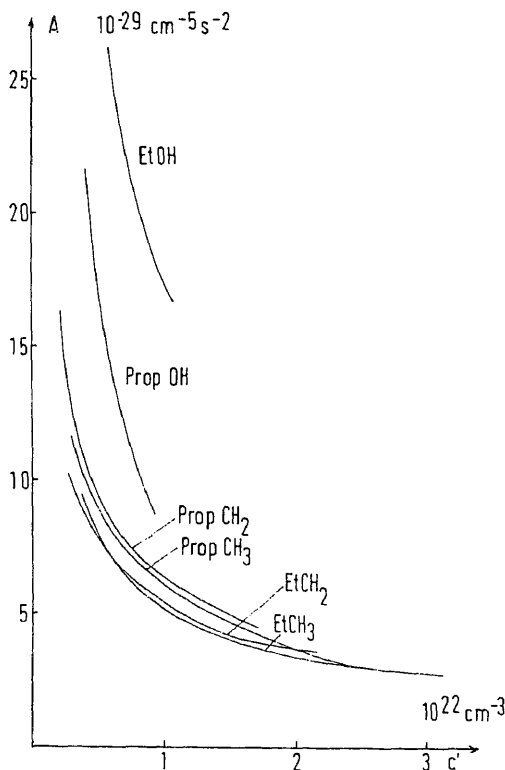


Figure 5. The association parameter A for the various ^1H atoms of ethanol (Et) and propionic acid (Prop) in their mixtures with CCl_4 as a function of the ^1H number density. The other corresponding hydrogen atoms of the H-bonding molecules are deuterons.

introduction in connection with (3) have to be applied. The displacement of a given OH proton from intramolecular bond partner oxygen requires little energy, this has the consequence that the acidic proton exchanges with those of the solvent water and thus for this proton no information about A can be obtained. However, by suitable isotopic substitution the methylene and methyl protons can be studied separately and in all cases association for the H atoms located in the various groups as defined above has been detected. Usually the systematic trend of the observations is such that for those CH protons closest to the carboxylic group the increase of A with decreasing acid concentration is strongest. Thus the methyl hydrogen of propionic acid shows only a fairly weak association effect. This, of course, means that the hydrocarbon parts of the acid molecules have an appreciable amount of freedom to move around the more tightly coupled carboxylic group, however it should be kept in mind that the so called hydrophobic interaction should introduce a tendency to bring the hydrocarbon parts of the molecule in contact (Franks 1975). It is clear that in the present system a short cut distinction, between what contribution of the observed association effect has to be attributed to the H-bonding in the carboxylic group and which to the hydrophobic interaction, cannot be made. But it has been found that CH_3 association in $\text{H}_2\text{O} + \text{butyric acid}$ is stronger than CH_3 association in $\text{H}_2\text{O} + \text{propionic acid}$ which is indeed a confirmation of the hypothesis of hydrophobic association: the larger the hydrocarbon part of the molecule, the stronger is the association.

There are quite a number of investigations dealing with mixtures of carboxylic acids with non-aqueous solvents, we quote the following systems: $\text{CH}_3\text{CH}_2\text{COOH}/\text{CCl}_4$ (Bender and Hertz 1977), $\text{CH}_3\text{COOH}/\text{CCl}_4$ (Berg *et al* 1976), $\text{CH}_3\text{COOH}/\text{C}_6\text{H}_{12}$ (Capparelli *et al* 1978), $\text{HCOOH}/\text{CCl}_3\text{H}$ (Kratochwill and Hertz 1977). In these solvents there is no exchange of the acid protons with the solvent protons, so that A can also be studied for the OH protons. In all cases the behaviour is as expected—there is a strong increase of A as the acid concentration decreases. It is interesting to note that in the solvent cyclohexane $\text{CH}_3\text{—CH}_3$ association seems to be fairly weak, whereas in the system $\text{CH}_3\text{COOH}/\text{CCl}_4$ such an association has been observed (Capparelli *et al* 1978, Berg *et al* 1976). The association of the CH_3 group in CCl_4 solution has been interpreted as a folding of the acid dimers such that the two acid molecules which are connected *via* the H-bond do not form a planar arrangement as it is usually represented in the classical treatments, rather the two 'methyl ends' of the H-bonded 'double molecule' approach towards each other such that one gets a V-shaped molecular system. In the more inert solvent C_6H_{12} this degree of folding or bending of the double molecule is less. Apart from this particular observation the other A values so far available for the carboxylic acids give essentially qualitative information so that we refrain from a detailed discussion or comparison of these numbers.

Also for systems in which one of the components forms weak H-bonds or in which no H-bonding occurs, association has been detected. So it has been found that chloroform-chloroform association exists in the mixture of CCl_3H with acetone (Capparelli *et al* 1976) and with dioxane (Helm and Kratochwill 1978), the association was detected *via* an increasing A coefficient for the H atom of chloroform as $\text{C}_{\text{CCl}_3\text{H}} \rightarrow 0$. In the mixture dimethylformamide-benzene ($\text{DMF}/\text{C}_6\text{H}_6$) association of the DMF molecules has been observed as well (Hertz *et al* 1976). The behaviour of the A coefficient reflecting DMF-DMF association is shown in figure 6. It should be noted that in the systems we quoted for that component we did not mention that the A coefficient usually remains constant

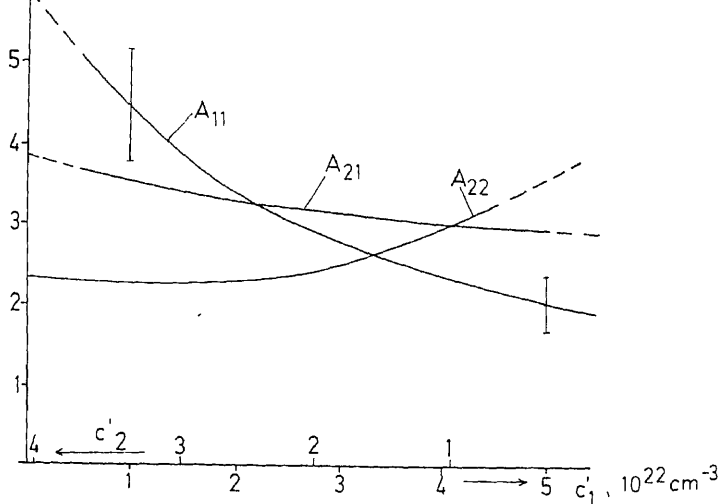


Figure 6. The association parameters A_{11} (DMF-DMF), A_{12} (DMF- C_6H_6), and A_{21} (C_6H_6 - C_6H_6) in the binary mixture dimethylformamide-benzene. c'_1 and c'_2 are the number densities of the DMF and C_6H_6 protons respectively. $T = 25^\circ C$.

absent or it is so weak that the uncertainty of the experimental method in its present state does not allow any definite statement.

4.3 Association between unlike molecules as detected by the A coefficient

We are now going to discuss the association between unlike molecules in a binary mixture. The intermolecular relaxation rate of a proton (or set of protons) residing on the molecule of kind 1 and being caused by the magnetic dipole-dipole interaction with all or selected protons on molecule 2 has also been studied. Now we are interested in the quantity n_{12} , the first (intermolecular) coordination number of atom 1 with respect to atom 2. Here atom 1 means any atom of the molecule forming component 1 and likewise, atom 2 means any atom on molecule 2. The protons on a given molecule may be equivalent or not, depending on the special system, so if one defines a first coordination number n_{12} , one has to give the necessary specification in the corresponding case. Then we have

$$n_{12} = 4\pi c'_2 \int_a^\infty \delta_{12}(r) g_{12}(r) r^2 dr$$

where $\delta_{12}(r)$ is any one of the three defining functions we have introduced above. $g_{12}(r)$ is the pair correlation function between the (hydrogen) atoms 1 and 2. Of course, we have $g_{12}(r) = g_{21}(r)$, and since it is reasonable also to set $\delta_{12}(r) = \delta_{21}(r)$ we obtain the result

$$n_{21} = n_{12} \frac{c'_1}{c'_2},$$

$$n_{12}/c'_2 = n_{21}/c'_1 = (n_{12})_r = (n_{21})_r = 4\pi \int_a^\infty \delta_{12}(r)g_{12}(r)r^2 dr,$$

are equal for both species 1 and 2.

Now if $(n_{ij})_r$ increases with decreasing concentration of species j , then we say that we have association of atom j with atom i , and on the other hand, if $(n_{ij})_r$ decreases with decreasing concentration of species j , then we have association of atomic species i with atom j . Of course, if $(n_{ij})_r$ remains constant over the entire composition range, then i - j (or A - B) association is absent. In full correspondence to the arguments given above we may again define a A_{ij} parameter, so that we have

$$A_{ij} = \left(\frac{1}{T_1} \right)_{i, \text{inter}}^{(j)} \cdot \frac{\bar{D}}{c'_j}, \quad (52)$$

where $(1/T_1)_{i, \text{inter}}^{(j)}$ is the intermolecular relaxation rate of the nucleus i caused by the magnetic dipole-dipole interaction with the atomic species j on the molecule of the other mixture component. As above, $\bar{D}$ is the mean self-diffusion coefficient of the two mixture components

$$\bar{D} = \frac{1}{2}(D_1 + D_2),$$

where D_1 and D_2 are the self-diffusion coefficients of molecules 1 and 2, respectively. In (52) the intermolecular relaxation rate is given by the expression

$$\left(\frac{1}{T_1} \right)_{i, \text{inter}}^{(j)} = \frac{1}{3} \gamma_i^2 \gamma_j^2 \hbar^2 \frac{n_{ij}^*}{a^4 \bar{D}}, \quad (53)$$

which is almost the same as (48), γ^4 is replaced by the product of the squares of the two gyromagnetic ratios and (48) has been multiplied by the factor $2/3$ because now we have the interaction between two unlike spins. The gyromagnetic ratios may be effectively equal if we are working with two nuclei of the same kind, however being non-equivalent due to the effect of the chemical shift. For unlike spins (37) may be modified in the same way

$$\left(\frac{1}{T_1} \right)_{i, \text{inter}}^{(j)} = \frac{1}{3} \frac{\gamma_i^2 \gamma_j^2 \hbar^2}{\bar{D}} \left[\frac{n_{ij}}{a^4} + \frac{4\pi}{3} \frac{c'_j}{b} \right]. \quad (54)$$

Equations (53) and (54) both refer to a situation where the two interacting nuclei have a spin $I = 1/2$, in the more general case the formulas have to be multiplied by an appropriate factor $4S(S+1)/3$ where S is the spin of the nucleus causing the relaxation effect.

Considering (52), (53) and (54) we get for the association coefficient A_{ij}

$$A_{ij} = \frac{1}{3} \gamma_i^2 \gamma_j^2 \hbar^2 \frac{(n_{ij}^*)_r}{a^4} \quad (55)$$

or

$$A_{ij} = \frac{2}{3} \gamma_i^2 \gamma_j^2 \hbar^2 \left[\frac{g(n, k, l)}{2a^4} (n_{ij})_r + \frac{2\pi}{3} \frac{c'_j}{b} \right]. \quad (56)$$

unlike molecules (AB association) has been studied, the first point which is to be stated is that A - B association has usually been found to be much weaker than association between equal molecules. The first system to be studied was $\text{DMF}-\text{C}_6\text{H}_6$, where no A - B association was found and A_{12} was found to be constant over the entire composition range (Hertz *et al* 1976), but later, in a recent investigation (Holz and Hertz 1981) the experimental results for the self-diffusion coefficients were improved and it turned out that there exists a weak association of DMF with benzene. The corresponding A parameter is also shown in figure 6. In the next study it was shown that chloroform is associated with acetone (Capparelli *et al* 1976), and interestingly, it turned out that dioxane is associated with chloroform (Helm and Kratochwill 1978), thus here we have the reverse association behaviour. Finally, there seems to exist a weak association of pyridine with methanol (Helm and Kratochwill 1978).

5. The study of the relative orientation of molecules in the liquid

We begin this chapter with a reconsideration of the association parameter A which we have introduced in the preceding chapter. Let us assume that again we have a binary mixture consisting of components 1 and 2. However now a special situation occurs, for instance, molecule 1 carries two different kinds of protons which are 'chemically non-equivalent'. We denote the two kinds of protons as I and S protons, respectively. The symbols I and S stand for a set of protons which among themselves are equivalent and which are considered to be located at two respective representative positions within the molecule. For example, if we consider the compound $\text{CH}_3-\text{CH}_2\text{Br}$, then the three methyl protons are the I spins, the representative point giving their effective position is close to the carbon atom. Likewise, we have two methylene spins S , their effective position is at the centre of the vector connecting the two hydrogen atoms. In an exact sense, the effective position is given by the mean value of $1/r_i^6$, where r_i is the intermolecular distance between a reference spin with which the magnetic dipole-dipole interaction occurs and the i th member of the set I .

Now we perform a dilution experiment, that is, we study the quantity A_{II} as the concentration of the component 1 decreases. In order to obtain A_{II} alone in such an experiment, we replace the S proton spins by deuterons. Let us assume that A_{II} increases in this experiment, then we conclude that we have association with respect to the atomic species I . In the next series of measurements we switch the I protons off by applying the deuteron substitution technique and we obtain the concentration dependence of A_{SS} in the same way by progressive dilution of component 1. Now it may occur that A_{SS} remains practically constant, whereas A_{II} definitely increases, as already mentioned.

What is the meaning of this experimental finding? In a first step of interpretation we assume that a_{II} and a_{SS} , the closest distances of approach for spins I and S , respectively, remain constant throughout the entire composition range. Then our measurements of

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \frac{1}{2} \frac{\gamma^4 \hbar^2}{a_{II}^4 D} g_{II}(n, k, l) n_{II} + \delta_{II},$$

and

$$A_{II} = \gamma^4 \hbar^2 \left[\frac{1}{2a_{II}^4} g_{II}(n, k, l) (n_{II})_r + \frac{2}{3} \cdot \frac{\pi}{b} \right],$$

however, $g_{SS}(n, k, l)$ and $(n_{SS})_r$ which are given by the equations

$$\left(\frac{1}{T_1}\right)_{\text{inter}}^{SS} = \frac{1}{2} \frac{\gamma^4 \hbar^2}{a_{SS}^4 D} g_{SS}(n, k, l) n_{SS} + \delta_{SS}^*,$$

$$A_{SS} = \gamma^4 \hbar^2 \left[\frac{1}{a_{SS}^4} g_{SS}(n, k, l) (n_{SS})_r + \frac{2}{3} \frac{\pi}{b} \right],$$

remain constant. n_{II} and n_{SS} are the first coordination numbers of spin I and S , respectively, with respect to the same type of proton (II and SS). Thus we see that there is a 'movement' of spin I towards the reference spin I as we dilute component 1 causing a crowding of I around the reference spin I relative to the mean I concentration in the mixture. There is no such crowding around the spin S with respect to S . We can now, of course, also describe the situation by saying that there is a rotation of the molecule 1 relative to the reference molecule 1, as we perform the dilution experiment. A rotation means that the relative orientation of the two 1 molecules is changing. Next we must emphasize that in general we do not know exactly whether the closest distances of approach remain constant or not. Our experimental finding may also be interpreted in such a manner that a_{SS} becomes larger and at the same time $g_{SS}(n, k, l)$ becomes larger in a corresponding way was to leave A_{SS} constant, furthermore, a_{II} becomes smaller. Then it is even more evident that we are concerned with a rotation of the molecules relative to each other. It may also be argued in a similar way when we have only information about the A of one type of proton. Then, if we have reasons from any other source to state that the first coordination number with respect to any other point within the molecule, the 'centre of the molecule', say, remains constant, we can conclude that the increase of A gives evidence for a relative rotation or reorientation of 1 molecule as the dilution process is going on. Such a rotation has been postulated for chloroform-chloroform pairs in the mixture of chloroform with acetone (Capparelli *et al* 1976).

After the description of the concept of a rotation or reorientation of one molecule relative to the other one when the composition of a binary mixture is changed, the question arises, whether in a system with given composition—which is not supposed to change—the relative orientation of two molecules can be determined. What we have so far, are the two intermolecular relaxation rates $(1/T_1)_{II}$ and $(1/T_1)_{SS}$. Applying (37) we may derive the two closest distances of approach a_{II} and a_{SS} . Of course, this demands the knowledge of the $g(n, k, l)$ for the two respective atom-atom pair distribution functions. We recall that the parameter n described the steepness of the model atomic pair distribution function, and the steepness in turn is a measure for the strength and maximum depth of the effective intermolecular potential. For instance, if the S proton belongs to an OH group and the OH groups are coupled through an H-bond, then n will be a comparatively large number and consequently we have $g(n, k, l) \approx 1$ (see figure 4). On the other hand, if the spins I are the protons of a methyl group, then n will

fourth power in the expression for the experimental quantity $(1/T_1)_{\text{inter}}$ (see (37)). The final result one obtains for the closest distance of approach will only moderately be influenced even if $g(n, k, l)$ and the first coordination number have a fairly wide range of uncertainty.

However, even if the two closest distances of approach, a_{II} and a_{SS} are known, the problem of finding the relative orientation is not yet solved. This will be seen in figure 7. In this figure the molecule is schematically drawn as a rod, at the two ends of the rod the two spin sets I and S reside, let the length of the rod be r_{IS} . Then we construct two circles with the radii a_{II} and a_{SS} around the two end points I and S respectively. We select any point on the circle with radius a_{II} . Let this point be the location of the spin I of the other molecule. Then that point on the circle with radius a_{SS} around S which has the distance r_{IS} from the original point on the circle a_{II} is a possible pair configuration leading to the pair of closest distances a_{II} and a_{SS} . A corresponding construction is shown in figure 7. It will be seen that there is an infinity of pair partner rods all of which have the same occurrence probability. For the relative orientation of maximum occurrence probability we need more information. This additional information will be supplied by a third intermolecular relaxation experiment. The next series of experiments is performed in such a way that the contribution $(1/T_1)_{\text{inter}}^{IS}$ to the relaxation rate of spin I is determined which is caused by the intermolecular magnetic dipole-dipole interaction of spin S with spin I . This may not require partial deuteration of the molecules investigated, depending on the kind of the system. In the same way, the contribution to the relaxation rate of spin S caused by the intermolecular dipole-dipole interaction with spin I may also be evaluated to obtain the relaxation rate $(1/T_1)_{\text{inter}}^{SI}$. And, of course, taking into account the relative numbers of spins I and S , the two results should be internally consistent. Before, the intermolecular relaxation rate $(1/T_1)_{\text{inter}}^{IS}$ is given by the relaxation

$$\left(\frac{1}{T_1}\right)_{\text{inter}}^{IS} = \frac{4}{9} \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \left[\frac{n_{IS}}{D a_{IS}^4} g_{IS}(n, k, l) + \frac{\pi c'_S}{3bD} \right]$$

and the proper estimate of n_{IS} and $g_{IS}(n, k, l)$ yields a_{IS} , the closest distance of approach between the spins I and S . Of course, we must have $a_{IS} = a_{SI}$. If now the a_{IS} value is available, the further construction procedure is as shown in figure 8. One draws two circles with radius $a_{IS} = a_{SI}$ around the locations of the two spins I and S .

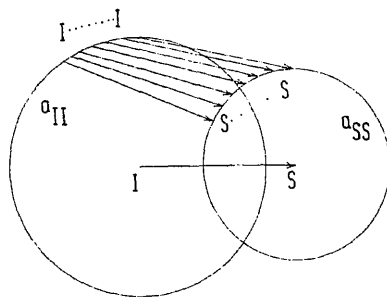


Figure 7. A number of I - S rod-rod configurations, having all the same closest distance of approach a_{II} and a_{SS} .

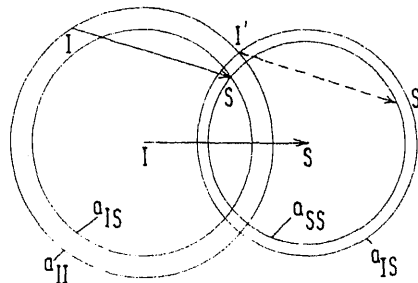


Figure 8. Circle construction to find two equivalent I - S rod-rod configurations of maximum occurrence probability, when the three closest distances of approach a_{II} , a_{IS} , and a_{SS} are given.

reference rod. The point of intersection between the circles a_{II} and a_{SS} obviously is a possible location of the spin S of the pair partner rod. Since for this partner rod the spin I , when it comes closest to the spin I of the reference rod, must lie on the circle a_{II} , and at the same time it must have a distance r_{IS} from the point of intersection a_{SI} a_{SS} , and so the relative orientation of the two molecules are found as shown in figure 8. But there is another equivalent relative configuration, namely, the point of intersection between the a_{IS} around S and the circle a_{II} is also a possible position of the spin I of the pair partner rod. Again, the spin S of the partner rod must lie on the circle a_{SS} and a distance r_{IS} apart from the point of intersection just mentioned. This gives the pair configuration which is indicated by the dashed arrow in figure 8. The model atomic pair distribution function as shown in figure 2 and written down as (36) has the property that the distance of closest approach is also the distance of maximum occurrence probability. As a consequence, the two equivalent rod configurations shown in figure 8 are also configurations of maximum occurrence probability. Of course, there is an infinite number of pair configurations which may also occur, however, their occurrence probability is smaller. A more detailed description of the method has been given elsewhere (Hertz 1976), only some further general aspects should be mentioned here.

According to the scheme of construction to find the pair configuration of maximum occurrence probability the corresponding distribution should have cylindrical symmetry around the axis of the reference rod IS . However, in many cases the shape of the molecules renders such a cylindrical symmetry impossible. There may, for instance, be a bromine atom below the line connecting the spins I and S in figure 8. This would lead us back to our example of the ethyl-bromide molecule. And in figure 8 it has been assumed that such an atom or a more bulky functional group is indeed present, and therefore the probability of finding the partner molecule below the rod in the same configuration as above the reference molecule, is zero.

In figures 9-14 we give a number of examples for pair configurations of maximum occurrence probability which have been derived from intermolecular nuclear magnetic relaxation rates. The relation of these pictures to the scope of this article, namely the study of intermolecular interactions, is given by the fact that any alteration of the pair configurations away from those shown in the figures require the delivery of work, *ie* the configurations shown should correspond to a minimum of effective potential energy. Finally, we mention that three dimensional pair configurations of maximum occur-

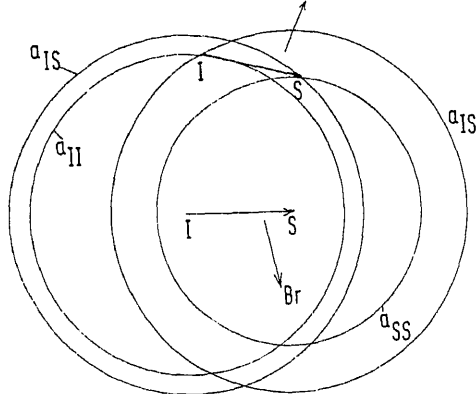


Figure 9. Pair configuration of maximum occurrence probability for C_2H_5Br , as constructed from a_{1I} , a_{1S} , and a_{SS} . Here, by accident the two equivalent configurations shown in figure 8 are identical. Arrows pointing towards Br indicate electric dipoles in a schematic way (Hertz 1978).

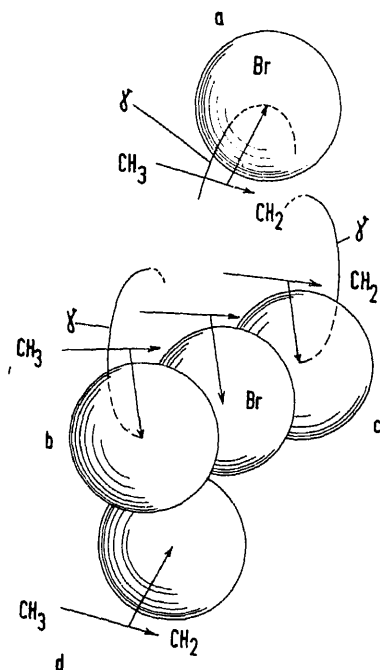


Figure 10. Various pair configurations of maximum occurrence probability derived from figure 9 as a visualization. The picture is to be understood in the following way: the maximum probability assigned to the pair: a-central molecule refers to the situation where all other molecules may have any configuration relative to the central one. Likewise, if the pair b-central molecule is fixed, then the other molecules may have any configuration. The angle γ may always have any value in the range indicated. Configurations b and c are equivalent, pair partner d is so distant from the central molecule, that proton-proton interaction does not contribute to relaxation rate (Hertz 1978).

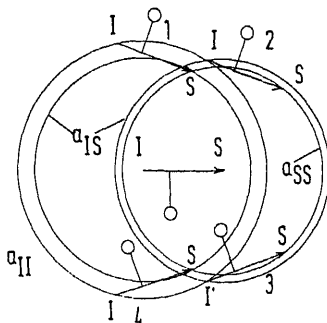


Figure 11. Various configurations of maximum occurrence probability for formic acid in the pure liquid. *I* and *S* are the formyl and carboxyl protons, respectively. We have presented a special case of a planar configuration and the small circles schematically indicate the carbonyl oxygen (Kratochwill and Hertz 1977).

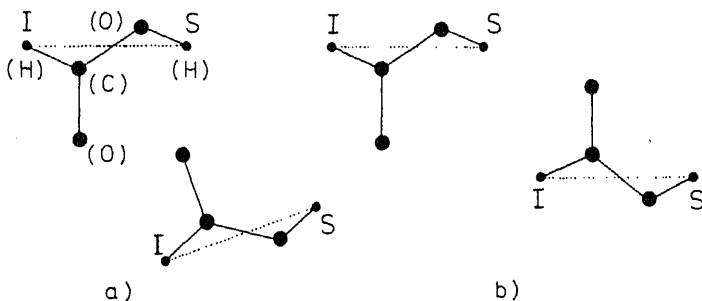


Figure 12. (a) Configuration 3 corresponding to that given as no. 3 in figure 11 showing the real molecular skeleton, (b) Selection of chainlike structure according to x-ray data of liquid formic acid (Kratochwill and Hertz 1977; Geisenfelder and Zimmermann 1963).

6. The intramolecular relaxation rate as a tool to study intermolecular interactions

6.1 Some general remarks

We return to (10) where the microscopic density self-correlation function of atom 2 relative to atom 1 was written as a product of the pair distribution function $p(\mathbf{r}_0)$ and the propagator $P(\mathbf{r}_0, \mathbf{r}, t)$. We had stated that $p(\mathbf{r}_0)$ and $P(\mathbf{r}_0, \mathbf{r}, t)$ are both determined by the nature of the intermolecular forces. In a more general situation we can also say that both these quantities are determined by the interatomic forces. Here the most well known type of atomic interaction is the formation of a molecule. Now $p(\mathbf{r}_0)$ has an intramolecular contribution which is given by the structure of the rigid or partly rigid molecule. This part of $p(\mathbf{r}_0)$ when we disregard for a moment the atomic vibrations,

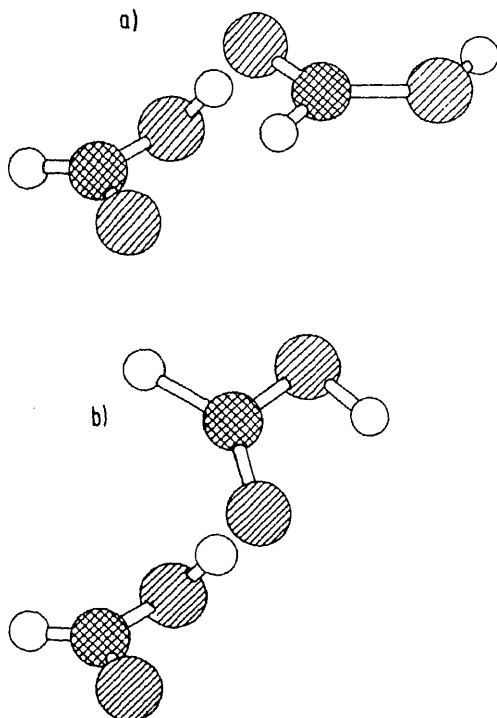


Figure 13. Perspective graphs of the pair of configurations of maximum occurrence probability. (a) Slightly modified configurations as given as no. 3 in figures 11 and 12, (b) Similar configuration, however electric dipole moments are parallel to give high Kirkwood g factors. Rotation about axis in (a) leads to configuration (b) (Kratochwill and Hertz 1977).

this contribution is not of direct interest to us. However, even if the molecular sizes and masses of two compounds are almost equal, it happens that the function $P(\mathbf{r}_0, \mathbf{r}, t)$ is markedly different. For instance, the molecules of ammonia and water are almost equal when mass and intramolecular distances are considered. Yet the quantity $P(\mathbf{r}_0, \mathbf{r}, t)$ which is a δ -function at $t = 0$ in NH_3 spread out in rotational space (the spherical surface of unit radius) to become uniform ($= 1/4\pi$) after a much shorter time than it does in water. This particular feature, of course, is a manifestation of the intermolecular forces and in the present chapter we deal with those aspects of the intramolecular relaxation rate which, as we suppose, are a consequence of the intermolecular forces.

When we said that $P(\mathbf{r}_0, \mathbf{r}, t)$ changes from a δ -function on a unit sphere to $P(\mathbf{r}_0, \mathbf{r}, t) = 1/4\pi$ as $t \rightarrow \infty$ we already implicitly stated that in the case of intramolecular motions the propagator is of purely rotational form. This must be so because within the molecule all the interaction distances apart from vibrations have constant values, so that only the orientation can change with time. In a polyatomic molecule there are many different vectors connecting two magnetically interacting nuclei. Now it is fairly evident that the rotational motion of the various vectors will be the same if the vectors are all physically indistinguishable due to the high symmetry of the molecule. If all

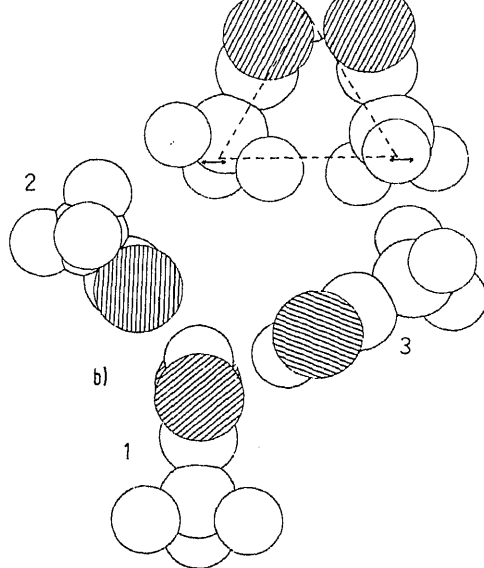


Figure 14. (a) Acetic acid dimer in a state of folding in the mixture with CCl_4 ($x_{\text{acid}} 0.1$). The experimental uncertainty is indicated by the two double arrows, (b) Molecular arrangement in pure acetic acid; molecules 2 and 3 are above and below molecule 1, respectively. This figure should be understood in the same way as explained in connection with the CH_3Br pairs in figure 10 (Berg *et al* 1976).

the present chapter which is more on an introductory level, we shall only treat the molecular motion as representing isotropic rotational diffusion even if the molecule has not the symmetry which necessarily demands isotropy of the motion. In the next chapter the emphasis will be on the anisotropic character of the rotational motion.

For the intramolecular magnetic dipole-dipole interaction between two spins, the time correlation function describing the change of the positional and rotational coordinates is

$$G(t) = \frac{1}{4\pi} \frac{1}{r_0^6} \int Y_2(\Omega_0) Y_2(\Omega) P(\Omega_0, \Omega, t) d\Omega_0 d\Omega. \quad (57)$$

It will be seen that this is essentially (17), however three modifications have been introduced: $p(\mathbf{r}_0)$ is replaced by $1/4\pi$, the probability density of finding a given orientation Ω_0 of the spin-spin vector. Ω_0 and Ω are the orientations of the vector at $t = 0$ and $t \geq 0$, respectively, they are given by the pair of angles θ and ϕ . Finally, the propagator is written in terms of orientation alone and r_0 is a constant quantity not changing with time. Then, if one introduces (57) in (15) and (14) and considers only the case of extreme narrowing, one obtains the result

$$\left(\frac{1}{T_1} \right)_{\text{intra}} = \frac{3}{2} \frac{\gamma^4 \hbar^2}{r_0^6} \tau_c. \quad (58)$$

In order to get a clearer understanding of the concept of the rotational correlation time τ_c it is instructive to compare this quantity with the reorientation time τ_r of a molecule in the liquid. τ_r is the time after which the proton-proton vector has changed its direction by *ca* 180°. Actually, the strict definition of the reorientation time is somewhat different, but for the qualitative purpose which is the intention here, the description given suffices. The reorientation time of the molecule is approximately equal to the dielectric relaxation time (Hasted 1972). We can also say that the intersection point of a vector fixed in the molecule with the unit sphere performs an erratic motion. Now the elementary steps of the rotational path on the unit sphere may be very small, in this event we speak of micro-step diffusion, or they may be larger, implying free paths of 90°, say, in such cases we would speak of rotational jump diffusion. The motion we have to assign to molecules undergoing fairly strong intermolecular interactions is closer to the former type and in particular we may assume that for the reorientational motion of H-bonded molecules the micro-step process is generally the better description of reality.

In the case of micro-step rotational diffusion the valid relation is

$$\tau_c = \frac{1}{3} \tau_r. \quad (60)$$

As the rotational steps become larger, $\tau_c \rightarrow \tau_r$, but for the present article it is sufficient to identify the rotational correlation time as one third of the reorientation time of the molecule considered. We give a brief indication why the factor 1/3 occurs in (63). In the situation of microstep rotational diffusion the propagator as given in (31) and used in (57) describes the motion of the vector. Due to the orthogonality relations of the spherical harmonics of the second degree in (16) all terms of (31) except the one belonging to $l = 2$ drop out. For the electric dipolar relaxation the $Y_2(t)$ are replaced by the spherical harmonics of first degree $Y_1(t)$, and consequently one is left only with terms corresponding to $l = 1$ after the averaging process. Now the respective correlation or reorientation time is given by the relation

$$\frac{1}{\tau_l} = l(l+1)D_r.$$

Thus we have $l(l+1) = 6$ and $l(l+1) = 2$ in the two cases and the ratio $\tau_c/\tau_r = 1/3$.

The molecule may contain several proton-proton vectors the relaxation contributions of which are observed simultaneously. Still let us assume that the motion is sufficiently isotropic. Then in a fair approximation the total observed intramolecular relaxation rate is given by the relation

$$\frac{1}{T_1} = \frac{1}{v} \sum_{i < j} \frac{2}{T_{ij}} \quad (61)$$

v is the number of like spins—here usually protons—in the molecule. T_{ij} is the relaxation time one would calculate for the spin pair formed from spins i and j according to (58) and the sum includes all pairs of like spins in the molecule.

Equations (58) and (61) apply when the magnetic dipole-dipole interaction between two or more protons is the relaxation mechanism. The deuteron has spin $I = 1$ and thus

it possesses a nuclear quadrupole moment which interacts with the electric field at the position of the nucleus. The electric field gradient is connected with the electron cloud of the molecule. Usually the relaxation rate caused by quadrupole interaction dominates over the magnetic effect to be expected from the nucleus with spin $I > 1/2$, this is also true for the deuterons. From the theory one obtains the formula (Abragam 1961; Farrar and Becker 1971; Slichter 1980)

$$\frac{1}{T_1} = \frac{3}{40} \frac{2I+3}{I^2(2I-1)} \left(1 + \frac{\eta^2}{3}\right) \left(\frac{eQ}{\hbar^2}\right)^2 q^2 \tau_c. \quad (62)$$

Here Q is the electric quadrupole moment, e is the charge of the proton, q is the maximum electric field gradient, η is an asymmetry parameter of the electric field gradient which in most cases is neglected. τ_c is the same correlation time which appears in (58) and (61) if the rotational motion is isotropic. Use of (62) has the advantage that the experimental relaxation rate is the intramolecular relaxation rate $1/T_1 = (1/T_1)_{\text{intra}}$, it has the disadvantage that one has to know the quadrupole coupling constant $eQ/h \cdot q$ in order to calculate τ_c which is not always an easy matter (Lucken 1969).

6.2 A model to connect the orientational correlation time with the intermolecular forces

As was already mentioned, H-bonding is the most important type of intermolecular interaction which can be studied by the intramolecular relaxation rate, as may be intuitively expected. A more detailed report about the various systems which have been studied has been given elsewhere (Hertz and Zeidler 1976), so here we shall only give a brief description of the basic ideas underlying the treatment and some representative experimental examples. For more detailed information the reader is referred to Hertz and Zeidler (1976). A molecule which is H-bonded to its neighbours has a longer rotational correlation time than a non-H-bonded molecule of comparable size and mass. Also the self-diffusion coefficient of such a molecule will be smaller. This is understandable because the rotational motion is determined by the angular dependence and the translational motion by the radial part of the intermolecular potential. Very often the depths of these potentials do not differ very much. Thus, all facts which we now describe as regarding rotational diffusion have their analogous in the translational form of motion which also gives us the justification to quote and discuss the self-diffusion coefficients when corresponding data are available. It has been briefly mentioned above that self-diffusion coefficients can also be obtained by the NMR method.

Our starting point is the well known Debye relation (Abragam 1961; Andrew 1956; Pople *et al* 1959).

$$\tau_c = \frac{4\pi r^3 \hat{\eta}}{3kT}. \quad (63)$$

The radius of the molecule in question is r . We assume that the shape of the molecule does not deviate too much from a sphere. $\hat{\eta}$ is the effective viscosity, it is usually smaller than the macroscopic viscosity of the liquid, it is often called the microviscosity, in itself it is not a well defined quantity. Here we define $\hat{\eta}$ in terms of (63), that is, it connects the experimental quantity τ_c with the molecular radius r . This procedure implies that r is

Next imagine that for a given system the H-bonds are 'switched on'. We observe that τ_c becomes longer. The reason is clear, since a set of molecules which are connected by a certain arrangement of links or bonds now acts as if it were one larger molecule, in other words the radius r of the monomeric molecule has to be replaced by the radius r^* of the aggregate which of course is greater, $r^* > r$. Now we can rewrite (63) to give

$$\tau_c = \frac{4\pi(r^*)^3 \hat{\eta}^*}{3kT} \quad (64)$$

$\hat{\eta}^*$ is the microviscosity for the H-bonded liquid and since we said that η increases with increasing particle size, we get $\hat{\eta}^* > \hat{\eta}$.

Next we ask: In what way is the effective radius r^* connected with the actual radii of the H-bonded aggregates? In the present situation the correlation time is usually of the order of 10^{-11} sec. Thus if the aggregate behaves like a stable molecule for a time longer than 10^{-11} sec, then with respect to the observation time implied in τ_c it is indistinguishable from a stable molecule. Furthermore, in general we have an association equilibrium involving aggregates composed of varying numbers of particles n . During the process of the relaxation of the nuclear magnetization, a given individual molecule for many times is a member of *each* aggregate of type n . Under these conditions, as the theory shows (Zimmerman and Brittin 1957), the third power of the effective radius of the molecule, r^* , equals the mean third power of the radius of the aggregate (see (67))

$$(r^*)^3 = p_0(\Delta E(\tau_c))(r^0)^3 + p_1(\Delta E(\tau_c))r_1^3 + p_2(\Delta E(\tau_c))r_2^3 + \dots \quad (65)$$

p_1 is the probability that a given molecule is H-bonded to one neighbour, p_2 is the probability that it is bonded to two neighbours, and so on. Of course we have

$$p_0 + p_1 + p_2 + \dots = 1$$

But as we pointed out, the validity of (65) is coupled to the condition that $\tau_h \gg \tau_c$, *ie* the lifetime τ_h in a given (n -fold) bound state must be longer than the correlation time τ_c (Hertz 1970). We may write

$$\tau_h = \tau_0 \exp(-\Delta E/RT) \quad (66)$$

$\tau_0 \approx 10^{-14}$ sec, thus for $\tau_h \gg 10^{-11}$ sec we obtain $\Delta E \lesssim -18.8$ kJ/mole. Therefore, we have added the parentheses with $(\Delta E(\tau_c))$ at the p_i 's in order to give the correct classification of what we mean by the word aggregate. We note that the quantity ΔE denotes the potential depth (*ie* it is a negative quantity) between two molecules in the presence of all the other molecules in the surrounding liquid, thus again it is an effective intermolecular potential. There may be aggregates for which $\Delta E > \Delta E(\tau_c)$. These aggregates contribute to $\hat{\eta}^*$, *ie* they are the reason that $\hat{\eta}^*$ also becomes greater apart from a certain repulsive contribution when the H-bonds are formed, this is the background effect. The situation just described, $\tau_h \gg \tau_c$ may be called the situation of slow exchange. Slow exchange means that the residence times in the various

Table 2. Some rotational correlation times and self-diffusion coefficients for non-H-bonded and H-bonded molecules.

Compound	Nucleus observed	Temperature (°C)	$(1/T_1)_{\text{intra}}$ sec^{-1}	τ_c (10^{-12} sec)	D ($10^{-5} \text{ cm}^2 \text{ sec}^{-1}$)	References
$\text{CH}_3\text{CD}_2\text{Br}$	^1H	25	0.032	0.67	3.9	Engelsmann <i>et al</i> (1974)
$\text{CD}_3\text{CH}_2\text{Br}$	^1H	25	0.020	0.84	3.9	Engelsmann <i>et al</i> (1974)
$(\text{CD}_3)_2\text{CO}$	^2H	25	0.20	0.47		Zeidler (1965); O'Reilly and Peterson (1971); Goldammer and Hertz (1970)
$(\text{CH}_3)_2=\text{CD}_2$	^2H	0	0.33	0.59	4.51	Mills and Hertz (1980)
$(\text{CH}_2)_4\text{O}$	^1H	25	0.021	0.57	—	Assink and Jonas (1970)
$\text{C}_3\text{D}_3\text{N}$	^2H	30	0.85	1.55	3.4	Zeidler (1965)
	^{14}N	25	606	1.86	1.9	Kintzinger and Lehn (1971)
C_6H_6	^1H	25	0.009	1.1	2.20	Holz and Hertz (1981)
						Zeidler (1965)
C_6H_{12}	^1H	25	0.051	1.2	1.7	Zeidler (1965)
NH_3	^1H	-71	0.064	0.66	—	Powles and Rhodes (1967)
CH_3OH	^{13}C	35	0.027	0.43		Lyarla and Grant (1972)
	^{17}O	25	240	4.3		Versmold and Yoon (1972)
CH_3OD	^1H	25	0.047	0.9		Goldammer and Zeidler (1969)
	^2H	25	3.23	4.4	2.2	Hertz and Zeidler (1976)
$\text{C}_2\text{H}_5\text{OH}$	^{17}O	25	649	11.6		Versmold and Yoon (1972)
$\text{C}_2\text{H}_5\text{OD}$	^1H	25	0.107	2.2	1.1	Goldammer and Zeidler (1969)
	^2H	25	7.14	9.8		Hertz and Zeidler (1976)
$\text{CD}_3\text{CH}_2\text{OH}$	^2H	25	1.06	2.6		Goldammer and Hertz (1970)
$\text{CH}_3\text{CD}_2\text{OH}$	^2H	25	0.862	2.1		Goldammer and Hertz (1970)
CH_3COOD	^2H	25	7.7	13		Berg <i>et al</i> (1976)
	^1H	25	0.157	3.0	1.1	Goldammer and Zeidler (1969); Hertz and Tutsch (1976)
CD_3COOH	^2H	25	0.76	1.8		Goldammer and Zeidler (1969)

indicated is

$$\left(\frac{1}{T_1}\right)_{\text{intra}} = \frac{2\pi\gamma^4\hbar^2\hat{\eta}^*}{kTr_0^6} [p_0(\Delta E(\tau_c))(r^0)^3 + p_1(\Delta E(\tau_c))r_1^3 + \dots] \quad (67)$$

and in fact (67) gives the justification for the averaging relation (65) (Zimmerman and Brittin 1957).

Let us now consider a liquid with weaker H-bonding for which

$$p_n(\Delta E(\tau_c)) = 0, \quad \text{for all } n \neq 0.$$

Now we have no aggregates which are long-lived as compared with the rotational correlation time. But still there are aggregates in the liquid, formally association can always be assigned to the molecular structure of a liquid and it is entirely a matter of our convenience which number for ΔE we choose for our classification: bonded aggregate—non-bonded single molecule. Thus it is equally well a possibility to choose $\Delta E \sim -RT$ as a line of demarcation between the states 'free' and 'bonded'. Now the life time of the corresponding aggregates is $10^{-13} \leq \tau_h \leq 10^{-12}$ sec, this is approximately the time after which the angular velocity correlation function has decayed to zero which has the consequence that we are just at the border line of the time scale in which a rotational diffusion coefficient can be defined, and since the coupled particles move together, a common diffusion coefficient may also be defined, at least qualitatively. The same argument is also valid for the translational self-diffusion coefficient. If we now have stated that the life time of the aggregate is short, as indicated above, so that it is smaller, in the limit very much smaller than the rotational correlation time τ_c and during the time τ_c a given molecule often or very often has changed its surroundings: free, coupled to one neighbour, coupled to two neighbours, free, coupled to three neighbours, coupled to one neighbour, free and so on. We have the situation of fast exchange relative to the correlation time τ_c . Again τ_c might act as the observation time *via* (58) and clearly we are unable to get any detailed dynamical information about the exchange process from a study of τ_c . We have fast exchange and thus only the mean value of the dynamical processes can be studied.

It may be shown (Beckert and Pfeifer 1965; Anderson 1967; Hertz 1967b; Anderson and Fryer 1969) that under the conditions of fast exchange the interconnection between the effective radius r^* occurring in (64) and the radii of the aggregates is given by the formula

$$(r^*)^{-1} = p_0(-RT)(r^0)^{-3} + p_1(-RT)r_1^{-3} + p_2(-RT)r_2^{-3} + \dots, \quad (68)$$

thus,

$$\frac{1}{\tau_c} = \frac{3kT}{4\pi\hat{\eta}^*} [p_0(-RT)(r^0)^{-3} + p_1(-RT)r_1^{-3} + \dots]. \quad (69)$$

All aggregates with $\Delta E > -RT$ contribute to the background effect $\hat{\eta}^*$. Together with a change of the repulsive contribution due to binding, they cause an increase of $\hat{\eta}^*$. In (68) and (69) we have again marked the probabilities by the boundary value $-RT$ which

has been used to define the nature of the aggregates. We see from (69) that again τ_c becomes longer when H-bonds are present, but the connection between the effective radius and the aggregate size has changed. Now

$$\left(\frac{1}{T_1}\right)_{\text{intra}} = \frac{2\pi\gamma^4\hbar^2\hat{\eta}^*}{kTr_0^6(p_0 \cdot (r^0)^{-3} + p_1 r_1^{-3} + p_2 r_2^{-3} + \dots)}. \quad (70)$$

Usually the direct application of (67) and (70) presents the following difficulty: If the monomeric particle is of spherical shape, then in general the higher aggregates will more or less deviate from spherical shape. Thus, each term would have to be corrected for anisotropic motion. However, the main purpose of these equations is to show that in the case of slow exchange (with respect to the correlation time τ_c) the correlation time is mostly influenced by the large aggregates whereas in the event of fast exchange it is mainly determined by the small aggregates.

6.3 Discussion of some experimental results

The interconnection between the rotational correlation time of a molecule as obtained from nuclear spin relaxation and H-bonding has been described fairly extensively in a previous review article (Hertz and Zeidler 1976), in which experimental results have also been presented and discussed. The number of new papers pertinent to this problem and appearing in the last four years is small. Thus it may suffice that in the present article we only give a brief summary of the experimental results, for more details the reader is referred to Hertz and Zeidler (1976). In the upper half of table 2 we present the rotational correlation times for a number of molecules in the corresponding pure liquid which do not form H-bonds. All these molecules are not spherical rigid bodies in the strict sense, however, they deviate as little as can be realized by the scheme of chemical bonding from such an ideal shape. Apart from ammonia these molecules have three to six heavy atoms, *ie* C, or O, or in one case Br. It will be seen that the correlation times ($= 1/3$ of the reorientation times) of these molecules range from 0.6 to 2 psec, the occurrence of internal motion in some of the examples should be noticed. The self-diffusion coefficient for these non-hydrogen bonded substances ranges from almost $2 \cdot 10^{-5}$ to almost $5 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$.

In the lower part of table 2 a number of data are collected which refer to molecules which again contain two to five heavy atoms which, however, form H-bonds. Now the rotational correlation times of the 'molecules' are definitely longer, they range from 4 to 60 psec. This clearly is the effect of the H-bonds, effectively the molecules have become larger. There exists one complication which we have already indicated by setting the word 'molecule' in quotation marks. Indeed, the values for the rotational correlation times refer to the H-bonded parts of the molecule in all cases, *ie* the OH groups. The alkyl part shows internal rotation, so that the correlation time of the methyl or methylene protons are shorter. Yet, again, when compared with the internal rotation-modified data of the non-hydrogen-bonded molecules, the times are longer which is an indirect manifestation of the H-bonding.

What we have found for the rotational motion is also verified for the translational diffusion, the self-diffusion coefficients in the case of H-bonding are about half those

the coupling of two spherical molecules with a bond we do not create a new spherical molecule. Thus, even if we can assign a suitable radius r^0 to the monomer this will not generally be possible for the dimer which will be more or less cigar-shaped. In this situation one can choose between two possibilities for proceeding further: One may have knowledge about the correlation time of a suitable model molecule for the dimer or trimer and so on. For example $(C_2H_5)_2CO_2$ (propyl acetate) has been taken as a model substance for the dimer of ethanol (Grüner and Hertz 1972). The other possibility is to estimate the correct values of $r_1, r_2, \dots$. An example is given in a paper by Weingärtner *et al* (1978), who studied the association between water and dimethyl formamide.

If we now have knowledge of suitable $r^0, r_1, r_2, \dots$ values then we can introduce these numbers in (67) or (70). The former equation is valid if the slow exchange limit represents the correct description, the latter section holds for the fast exchange situation (see the previous section). If the existence of aggregates containing many molecules cannot be excluded and still the increase of the relaxation rate relative to the monomeric state is not very great, then (70) is to be applied. This is the situation expected in pure water. In contrast to this, if in a given solution the occurrence of high aggregates is very unlikely and still an appreciable increase of the intramolecular relaxation rate with increasing H-bonding component has been observed, then the slow exchange formula certainly is the correct one. In this situation one can conclude that the potential depth of binding force is greater than the limiting energy necessary for a lifetime to be equal to the correlation time in question, *i.e.* -18.8 kJ/mole in the case where we have a correlation time of the order of 10^{-11} sec. This method has been applied to the mixture CCl_4 -ethanol at comparatively low ethanol concentrations (Grüner and Hertz 1972). Probably at higher concentrations of methanol and ethanol the exchange becomes faster and it is doubtful whether (67) is still valid because in the pure liquid large aggregates would lead to very large proton relaxation rates which have not been observed. On the other hand, it has been found (Göller *et al* 1972) that the intermolecular OH-OH relaxation rate in CD_3OH and C_2D_5OH can be calculated approximately correctly if one assumes that a proton-proton vector only performs rotational motion with a correlation time $\approx 10^{-11}$ sec. Such a model would imply that the life-time of the dimer is about 10^{-11} sec. *i.e.* it is not short compared to the correlation time. It should be emphasized that the method we have described so far has been applied only very rarely, and, particularly these days as owing to more modern equipment more reliable and precise experimental results can be obtained, a systematic application of the intramolecular relaxation method is strongly recommended.

As we already mentioned, the correct description of the dynamical situation in water is given by a fast or at least moderately fast exchange of the water molecule among aggregates containing two or more molecules. The residence time in a given state of aggregation is $\leq 10^{-12}$ sec. The rotational—and translational—diffusion is close to a microstep diffusion, though it probably does not really represent the ideal form of microstep diffusion. It has been calculated from $\tau_c = 2.5$ psec, the rotational correlation time in pure liquid water ($25^\circ C$), and from $\tau_{c0} = 0.5$ psec, the estimated correlation time of monomeric water in an inert solvent, that the probability ω_1^+ of finding a water

The p_i 's in (70) are suitable products of ω_i and $1 - \omega_i$, $i = 1, 2$. Furthermore, again from the comparison of τ_c in pure water and τ_{c0} for the unbound molecule, it has been estimated that the effective potential depth in liquid H_2O which couples two water molecules together for a time $\approx 10^{-12}$ sec is ≤ -9.6 kJ/mole (Hertz 1971). This result demonstrates again that in a qualitative way numerical results for the effective intermolecular potential can be derived from the study of intramolecular nuclear spin relaxation rates.

7. Anisotropic motion and intermolecular interaction

7.1 Evaluation of spectral densities and effective correlation times

In the following two sections we discuss the anisotropic rotational motion of small, rigid molecules as studied by nuclear magnetic relaxation rates. First we introduce briefly the theoretical framework. Recent work has demonstrated that the measurement of cross-correlation (dipolar) relaxation terms in addition to the familiar autocorrelation terms can provide valuable new information Redfield 1965. Therefore we quote here the formulas for dipolar relaxation in full generality—the meaning of the technical terms ‘auto- and cross-correlation’ will be explained in the text subsequently. We give a series of experimental examples arranged logically in three subsections, symmetric top molecules, asymmetric top molecules which have been treated approximately as symmetric tumblers, and finally planar asymmetric top molecules where a complete analysis of motional anisotropy has been performed.

In the previous chapters it has been discussed thoroughly that the time correlation function of a perturbation, or its associated Fourier-transform, the spectral density, is the central quantity relating the microscopic behaviour and the measurable relaxation rate. We illustrate the evaluation of spectral densities here for dipolar relaxation, and for the sake of notational simplicity we consider only spins $1/2$. In the dipolar relaxation mechanism we have to deal with fluctuating magnetic moments associated with individual spin pairs residing on one molecule. Basic relaxation theory (Abragam 1961) shows that a time correlation function of the so-called ‘lattice part’ $Y_2^{(m)}(\Omega_{AB}(t))/r_{AB}(t)$ has to be calculated. $Y_2^{(m)}$ is the m th component of a spherical harmonic of degree two. AB refers now to a spin pair $\mathbf{r}_{AB}(t)$ is an internuclear vector with the orientation $\Omega_{AB}(t)$ and the magnitude $r_{AB}(t)$. For intramolecular relaxation we have obviously $r_{AB}(t) = r_{AB}(0)$ if the vector is between two nuclei in a rigid molecule. When evaluating the time correlation function one has to include correlations between $Y_2^{(m)}/r$ for AB and $CD \neq AB$ pairs, see (71) below. The motional model used so far is the rotational diffusion model since it is the only one that allows the calculation of the time correlation function for asymmetric rotors for auto- and cross-correlation. To build a conceptual bridge to older work on the basis of the spherical rotor model effective correlation times may be conveniently introduced. For auto-correlation these τ_{eff} 's are associated in a pictorial interpretation with the motion in time of *one* internuclear vector—in the spherical model the τ_{eff} 's for *all* internuclear vectors in a rigid molecule are equal by definition. Cross-correlation ‘effective correlation times’ should be considered more as formal quantities; they may be < 0 and this obviously conflicts with the concept that the correlation time is a measure of the decay of the orientational correlation function.

Dipolar interaction (DD) is a tensor interaction of rank two. Likewise quadrupolar

anisotropic motion can be used a combination of τ_{eff} 's from DD and QF. To proceed we start with the time correlation function for dipolar interaction. AB and CD refer in the most general situation to two different spin pairs, $\mathbf{r}_{AB}(t)$ and $\mathbf{r}_{CD}(t)$ are the two internuclear vectors associated with them.

$$G(t) = N \frac{Y_2^{(m)}(\Omega_{AB}(0))}{r_{AB}^3(0)} \cdot \frac{Y_2^{(m)}(\Omega_{CD}(t))}{r_{CD}^3(t)}, \quad (71)$$

N is the normalization factor.

Here we have used the result that for correctly normalized lattice functions the correlation functions are independent of the component index q of the spherical harmonics $Y_2^{(m)}$ (Hubbard 1969) Ω_{AB} are the two Eulerian angles that describe the orientation of the vector $\mathbf{r}_{AB}$ in the laboratory frame. If we separate the ensemble average over vibration and rotation (71) changes to

$$G(t) = N \langle r_{AB}^{-3} \rangle_{\text{vib}} \langle r_{CD}^{-3} \rangle_{\text{vib}} \cdot \langle Y_2(\Omega_{AB}(0)) Y_2(\Omega_{CD}(t)) \rangle_{\text{rot}} \quad (72)$$

(correctly not r^{-3} but (Y_2/r^3) should be averaged, Diehl and Niederberger 1973).

Equation (71) is generally valid for dipole-dipole relaxation but (72) only for intramolecular relaxation if the magnitude of vectors $\mathbf{r}_{ij}$ is constant in time. Such a condition is met by internuclear vectors in a rigid molecule but generally not by vectors between a nucleus in an internally rotating group and a nucleus in the rigid 'backbone'. Obviously only angular functions determine $G(t)$. Expressions of the form of (72) with $AB \neq CD$ occur naturally in the complete theoretical treatment. They are denoted as 'cross-correlation' terms whereas for $AB = CD$ we have 'auto-correlation' terms. To perform the average $\langle \dots \rangle_{\text{rot}}$ in (72) we define the orientation of an internuclear vector $\mathbf{r}_{ij}$ in a molecule-fixed system. This is straightforward enough for rigid molecular systems. Complications because of additional degrees of freedom of internal rotation shall not be treated here (Woessner 1962a, b; Woessner *et al* 1969). A time dependent transformation connects the molecule-fixed with the laboratory system,

$$\begin{aligned} & \langle Y_2^{(m)}(\Omega_{AB}(0)) Y_2^{(m)}(\Omega_{CD}(t)) \rangle_{\text{rot}}^{\text{LAB}} \\ &= \sum_{n, n'} \langle D_{nm}^{(2)}(\Omega(0)) D_{n'm}^{(2)}(\Omega(t)) \rangle_{\text{rot}} Y_2^{(m)}(\Omega_{AB}^{\text{MOL}}) Y_2^{(m)}(\Omega_{CD}^{\text{MOL}}). \end{aligned} \quad (73)$$

Ω (without indices) are the Eulerian angles which relate the laboratory frame to the molecular frame, and $D_{mn}^{(2)}$ are elements of the Wigner rotation matrix. To evaluate the rot-average on the right-hand side of (73) one has to introduce a motional model. Microstep rotational diffusion is widely accepted (above all in the extreme-narrowing limit) and is also the only model that enables the calculation of cross-correlation terms. Hubbard (1970) and Huntress (1970) have first performed the (tedious) evaluation, and a recent reformulation has been given by Werbelow and Grant (1977). The full description contains the rotational diffusion-tensor or in its diagonal form the three rotational diffusion constants D_{ii} , $i = x, y, z$. Principal rotational correlation times are defined by

$$\tau_{ii} = \frac{1}{6D_{ii}}, \quad i = x, y, z, \quad (74)$$

where the numerical factor 6 stems from having calculated tensor quantities of rank two (see also §6.1). Only if the molecule-fixed coordinate system, introduced above,

coincides with the principal diffusional system the three constants D_{ii} give a correct description! (Here, of course, only the angular transformation is important, the origin of the centers is unimportant in the calculation of the correlation function. Ω_{AB}^{MOL} is the orientation of an internuclear vector $\mathbf{r}_{AB}$ with respect to any arbitrary coordinate system fixed in the molecule.) Otherwise nondiagonal elements D_{ij} , $i \neq j$ have to be included (Huntress 1970). The orientation of the principal diffusional axis system can be given by symmetry or its orientation to the molecular frame is an additional parameter. For molecules with symmetry C_{2v} or greater, the inertial tensor diagonalises also the diffusional tensor. The constants D_{ij} are statistical parameters which describe the 'average' behaviour of a single molecule, and therefore, in the ensemble equivalent parts of a molecule experience equivalent interactions with the environment.

We give finally the result in the situation of extreme narrowing (experimental work has been almost exclusively in this limit):

$$J \equiv J_{AB,CD} = 0, \quad 3 \langle r_{AB}^{-3} \rangle \cdot \langle r_{CD}^{-3} \rangle \tau_{AB,CD} \quad (75)$$

$\tau_{\text{eff}} = \tau_{ABCD}$ is the effective correlation time for the interaction of two spin pairs AB and CD . The full and lengthy expressions for τ_{ABCD} can be found in Vold and Vold (1978, eqs (35a)–(38d)). It is possible that other published tables (Vold *et al* 1977; Wright *et al* 1979) contain misprints. τ_{ABCD} is a function of the orientation of the two vectors $\mathbf{r}_{AB}$ and $\mathbf{r}_{CD}$ (4 angles) and the diffusion constants D_{ii} , $i = x, y, z$, in the principal diffusional axis system, i.e. the relative orientation of the diffusional axis system with respect to a molecular frame must be known. Three linear independent relaxation rates should allow the determination of the three coefficients D_{ii} . The practical application has revealed that due to the complicated angular dependence of the effective correlation times on the diffusion constants a large numerical uncertainty of the D_{ii} 's results, in particular if only auto-correlation terms τ_{ABAB} are used in the calculation of the diffusion constants. Recent work (Vold *et al* 1977; Vold and Vold 1978; Nery and Canet 1978; Stark *et al* 1979; Kratochwill *et al* 1979) has shown how this problem may be circumvented by including cross-correlation terms in the analysis.

Most of the experimental work has been done using simple models. For an isotropic model with

$$D_r = D_{xx} = D_{yy} = D_{zz}, \quad (76)$$

we have

$$\tau_c \equiv \tau_{\text{eff}} = \frac{1}{6D_r}. \quad (77)$$

One relaxation rate is sufficient to determine D_r . For the symmetric rotor model (Woessner 1962a, b) we obtain with

$$D_{\parallel} = D_{zz} \quad \text{and} \quad D_{\perp} = D_{xx} = D_{yy}, \quad (78)$$

$$\tau_{\text{eff}} = \frac{A}{6D_{\perp}} + \frac{B}{5D_{\perp} + D_{\parallel}} + \frac{C}{2(D_{\perp} + 2D_{\parallel})}, \quad (79)$$

where

$$A = \frac{1}{2}(3/2 - 1)^2$$

parallel motion. Equations (76)–(80) are valid for auto-correlation terms, *i.e.* the conventional relaxation rates. τ_{eff} is then formally given by τ_{ABAB} , and the time correlation function of *one* particular vector $\mathbf{r}_{AB}$ is considered. With the values of τ_{eff} we have the desired expressions for the longitudinal relaxation rate by substituting τ_c in (58) and (62) by τ_{eff} . According to (79) two (independent) relaxation rates allow the determination of the diffusion constants $D_{\perp}$ and $D_{\parallel}$.

For the sake of completeness and to illustrate the increased complexity we cite in table 3 expressions for effective correlation times in planar molecules. ϕ_{ij} is the azimuthal angle of the vector $\mathbf{r}_{ij}$ in the principal axis system. Δ_+ and Δ_- are two redefined motional parameters (Vold *et al* 1977). It is

$$\Delta_+ = \frac{D_{xx} + D_{yy}}{2D_{zz}} \quad (81)$$

(motional anisotropy)

and

$$\Delta_- = \frac{D_{xx} - D_{yy}}{D_{zz}} \quad (82)$$

(motional asymmetry)

For a determination of Δ_+ , Δ_- and D_{zz} three effective correlation times are necessary, one of these *has to be* connected with a cross-correlation term (J_{ABCD} , $AB \neq CD$).

The symmetric diffusive rotor model, (79) and (80), seems to be most appealing for experimental verification. It contains basic features of anisotropic motion and for the experimental analysis only two relaxation rates (auto-correlation) are needed. A study of symmetric top molecules ZX_3Y is of interest since for C_{3v} symmetry the orientation of the diffusion tensor is given by symmetry. Widespread application for molecules with less than C_{3v} symmetry has been dictated by practical reasons: it was often impossible to measure more than two independent relaxation rates. A very important class of chemical systems studied in this way are the planar aromatic six-membered rings. We consider monosubstituted benzenes as an example. Based on experimental results the ratio of ortho(meta)-/para-carbon relaxation rates constitute a convenient parameter to describe motional anisotropy:

$$\rho = \frac{1/2 [(1/T_1)_{\text{intra}}(\text{ortho}) - (1/T_1)_{\text{intra}}(\text{meta})]}{(1/T_1)_{\text{intra}}(\text{para})} \quad (83)$$

Table 3. Effective correlation times for planar asymmetric tumblers.

$\tau_{\text{eff}} \equiv \tau_{abcd} = \sum_{i=1}^3 c_i / \lambda_i$	$A = 1/2(1 + (1 - \Delta_+)/\Omega)$
$c_1 = 3/4 \sin 2\phi \sin 2\phi'$	$B = 1/2(1 - (1 - \Delta_+)/\Omega)$
$c_2 = 1/4 A + w_1 B + w_2 C$	$C = (3^{1/2}/2)\Delta_-/\Omega$
$c_3 = 1/4 B + w_1 A - w_2 C$	$w_1 = 3/4 \cos 2\phi \cos 2\phi'$
$\lambda_1 = 2D_{zz}(2 + \Delta_+)$	$w_2 = (3^{1/2}/8)(\cos 2\phi + \cos 2\phi')$
$\lambda_2 = 2D_{zz}(1 + 2\Delta_+ - \Omega)$	$\Delta_+ = (D_{xx} + D_{yy})/2D_{zz}$
$\lambda_3 = 2D_{zz}(1 + 2\Delta_+ + \Omega)$	$\Delta_- = (D_{xx} - D_{yy})/D_{zz}$
$\Omega = (1 + 3/4\Delta_-^2 + \Delta_+^2 - 2\Delta_+)^{1/2}$	$\phi = \phi_{ab}, \phi' = \phi_{cd}$

Assuming equal bond distances $\langle r_{\text{CH}}^{-3} \rangle^{-1/3}$ for all CH vectors the ratio of relaxation rates is equal to a ratio of correlation times,

$$\rho = \frac{1/2 [\tau_{\text{eff}}(\text{ortho}) - \tau_{\text{eff}}(\text{meta})]}{\tau_{\text{eff}}(\text{para})} \quad (84)$$

Woessner's equations, (79) and (80), can be used when the principal axis system is chosen as shown in figure 15a. The orientation of the principal axis system must be as shown from symmetry considerations. If we adopt *per definitionem* an equal in-plane (D_{yy}) and out-of-plane (D_{xx}) rotational diffusion constant (both $D_{\perp}$), two effective correlation times

$$\tau_{\text{eff}}(\text{ortho}) = \tau_{\text{eff}}(\text{meta}) \text{ since } \tau_{\text{eff}}(\theta = 60^\circ) = \tau_{\text{eff}}(\theta = 120^\circ)$$

and

$$\tau_{\text{eff}}(\text{para}) = \tau_{\text{eff}}(\theta = 0^\circ)$$

are sufficient to determine $D_{\parallel}$ and $D_{\perp}$. The equality

$$D_{xx} = D_{yy} = D_{\perp}$$

is a stringent demand, absolute values of $D_{\parallel}$, $D_{\perp}$ for asymmetric top molecules calculated with the symmetric rotor approximation may be quantitatively unsatisfactory.

On the other hand the ratio ρ is meaningful as a qualitative motional probe (we discuss this again for monosubstituted benzenes). In figure 15b we show the indexing of the axis system for the application of the equations valid for an asymmetric tumbler, see table 3. Here D_{zz} is the out-of-plane diffusion constant. Results of model calculations are shown in figure 16. As for the symmetric model we have $\tau_{\text{eff}}(o) = \tau_{\text{eff}}(m)$ and therefore only the ratio $\rho = \tau(o)/\tau(p)$ is shown. ρ is contained in a relatively narrow band for a large variation of the value of the third (out-of-plane) diffusion constant D_{zz} . $D_{zz}/D_{yy} = 1$ corresponds to the symmetric rotor model. For isotropy with respect to the ring plane, $D_{xx} = D_{yy}$, one calculates $\rho = 1$, independent of D_{zz} . $\rho \neq 1$ contains information on all three diffusion constants, but one given value is consistent with a family of triples (D_{xx} , D_{yy} , D_{zz})—defined by a horizontal cut through the band of curves in figure 16. (More generally, we will learn below when discussing specific examples that in planar systems, (auto-correlation) relaxation rates alone cannot give a value of D_{zz}

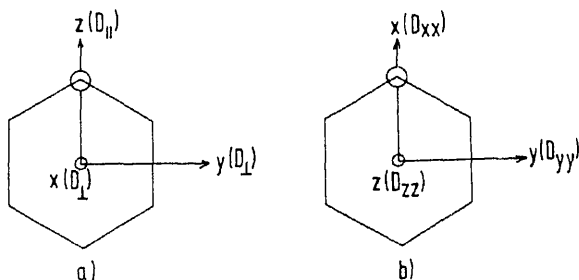


Figure 15. Conventional choice of indexing of axes for the model of (a) asymmetric rotor (b) an asymmetric rotor for planar molecules, in particular monosubstituted benzenes. The orientation of the principal diffusional axis system in monosubstituted benzenes is determined

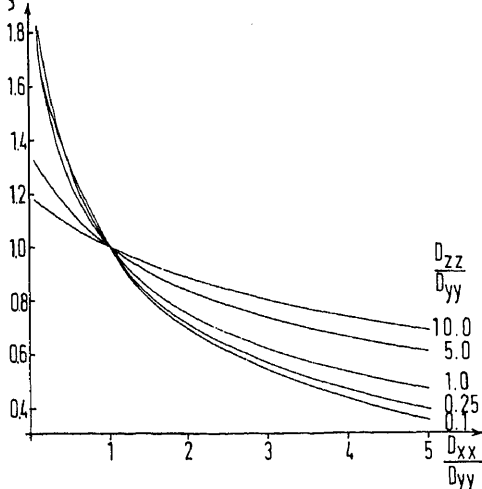


Figure 16. Motional parameter ρ as a function of the anisotropy ratio of the rotational diffusion constant D_{xx}/D_{yy} for various values of the out-of-plane rotational diffusion constant D_{zz} .

but only a precise figure for D_{yy}/D_{xx} , (Kratochwill and Vold 1980.)) If we are interested only in a qualitative evaluation the sign of $(\rho - 1)$ immediately indicates the anisotropy with respect to the ring plane, $\rho < 1$ means $D_{xx} > D_{yy}$, i.e. faster reorientation around the 1,4-axis for any arbitrary D_{zz} . Such values $\rho < 1$ have experimentally been found for 1-substituted benzenes where steric effects result in anisotropic motion or systems where strong intermolecular hydrogen-bonds can be formed.

To summarize the theoretical framework we have two important quantitative models to interpret relaxation rates in terms of anisotropic motion: the models of a symmetric and of an asymmetric (diffusive) rotor. For planar rings ratios of correlation times, or relaxation times respectively, can be used to obtain information about the motional anisotropy with respect to the ring plane, in favourable situations even quantitatively.

7.2 Experimental examples

To study the anisotropy of molecular reorientation one has to measure more than one effective correlation time associated with different vectors in the molecule under consideration. The most general situation, the asymmetric tumbler, can be evaluated if $n \geq 3$ independent effective correlation times τ_{eff} are known. It is favourable to refer to only one experimental method, i.e. in our case to base the analysis upon NMR relaxation rates alone. In principle correlation times being the result of other types of spectroscopy e.g. light scattering can be used in a combined analysis.

We shall first discuss symmetric tumblers; mono- or trisubstituted methanes are a convenient series of chemical compounds to shed light on the principles of the procedure. From molecular geometry the orientation of the rotational diffusion tensor is known and the symmetric model provides an exact description as long as rotational diffusion is accepted. Methylene compounds CH_2X_2 have been treated with the

were studied in the pure phase as well as in binary mixtures. Since internal rotation is not present these systems are convenient for studies of overall motional anisotropy. Such investigations provide information about the symmetry of the intermolecular potential. With conventional relaxation rates (auto-correlation) and with an approximate procedure (observation of the ratio of correlation times) meaningful qualitative results can be obtained. More refined methods allow a quantitative analysis as will be demonstrated below.

For symmetric top molecules ZX_3Y with C_{3v} symmetry Woessner's theory (Woessner 1962b) can be applied in a straightforward manner. Figure 17 shows the orientation of the principal axis system of the rotational diffusion tensor. The $\parallel$ -motion is around the figure axis (C_3) and $D_\perp$ describes the orientation of the figure axis. According to (79) and (80) the effective correlation time associated with a $Z-X$ vector depends only on $D_\perp$, the corresponding τ_{eff} may be determined by a $Z-X$ dipolar relaxation rate or a quadrupolar relaxation rate of the X nucleus. (Generally τ_{eff} associated with a vector parallel to one principal axis is determined by the two diffusion constants perpendicular to this direction.) τ_{eff} associated with a $Z-Y$ vector depends on $D_\parallel$ and $D_\perp$. Henceforth we have two equations to solve for the unknowns $D_\parallel$ and $D_\perp$. Experiments have been evaluated according to these lines. The analysis revealed that this model may be oversimplified. The calculated rotational diffusion constant $D_\parallel$ for the motion around the figure axis shows that the $\parallel$ motion is barely in the limit of small step angular diffusion but inertial effects are also important. The discussion of more refined models ('extended diffusion'), elaborated for spherical and symmetric rotors, is beyond the scope of this review. Essentially such models describe collision interrupted free inertial motion where either only the orientation (M -diffusion) or the orientation and the magnitude (J -diffusion) of the angular momentum vector are randomized in each 'collision' McClung 1977.

The anisotropic reorientation of acetonitrile has been investigated by Bopp (1967) and Woessner *et al* (1968) and ^{14}N and ^2H or ^1H relaxation rates used to determine $D_\parallel$ and $D_\perp$. Consistent results were obtained: the reorientation of the methyl group about its symmetry axis is approximately ten times faster than the reorientation of the nitrile group, see table 4. Different activation energies for $\parallel$ - and the $\perp$ -motion corroborate the statement that motional anisotropy exists. For the $\parallel$ -motion inertial effects are important as has been pointed out by Bull and Jonas (1970). The activation volume for $\parallel$ -motion, $\Delta V^\ddagger(D_\parallel)$, is ≈ 0 , and $\Delta V^\ddagger(D_\perp) = 8.5 \pm 1.4 \text{ cm}^3 \text{ mol}^{-1}$. The relative import-

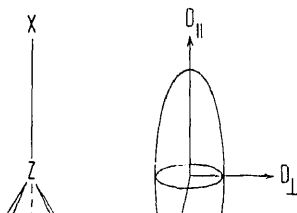


Table 4. Symmetric tumblers: anisotropy of motion and Arrhenius' activation energies (kJ mol^{-1}).

System	$D_{\parallel}/D_{\perp}$	$E_a(D_{\parallel})$	$E_a(D_{\perp})$	References
CH_3Br	≈ 8 (25°C)	3.8	7.1*	Lassigne and Wells (1977b)
CH_3I	10 (25°C)	3.3	7.9*	Gillen <i>et al</i> (1971)
CH_3CN	10.35 (25°C)	3.1	8.4	Woessner <i>et al</i> (1968)
CH_3CN	8.9 (25°C)	3.3	7.1	Bopp (1967)
$\text{CH}_3\text{C}\equiv\text{CH}$	14.1 (-30°C)	2.1	7.1	Jonas and DiGennaro (1969)
CH_3NO_2	≈ 9 (25°C)	3.8	7.9	Suchanski and Canepa (1979)
CH_3HgCH_3	≈ 40 (25°C)	5.4	3.6	Lassigne and Wells (1977a)
CHCl_3	1.9 (20°C)	2.9	6.7	Huntress (1969)
CHBr_3	1.5 (20°C)	7.5	10.5	Yamamoto and Yanagisawa (1977)
VOCl_3	1.4 (30°C)	9.6	8.2*	Gillen and Noggle (1970)
CCl_3CN	2.1 (25°C)	8.0	11.2*	Gillen and Noggle (1970)
BCl_3	0.75 (0°C)	6.9	5.3*	Gillen and Noggle (1970)

* Calculated from a hydrodynamic approach.

ance of the shape effect and the influence of the electric dipole on the motion could not be elucidated since the long axis of the molecular ellipsoid (shape) and the axis of the dipole moment coincide. Anisotropic motion was also found for the isoelectronic methylacetylene (Jonas and DiGennaro 1969). The anisotropy found $D_{\perp} = (13 \pm 1.5) \cdot 10^{10} \text{ sec}^{-1}$ and $D_{\parallel} = (183 \pm 12) \cdot 10^{10} \text{ sec}^{-1}$ at -30°C compares well with the anisotropy in acetonitrile. One is led to the conclusion that in both systems the molecular shape determines grossly the reorientational behaviour. Dipole forces $-\mu(\text{CH}_3\text{CN}) \approx 3.5 \text{ D}$ and $\mu(\text{CH}_3\text{CCH}) \approx 0.7 \text{ D}$ —are of minor importance at least when the additional degree of freedom of rotation around the C_3 -axis is present. Qualitatively Perrin's (1934) extension of the Debye-Stokes-Einstein hydrodynamic equations to ellipsoid-shaped molecules explains the observed anisotropy. With a ratio $b/a \approx 0.8$ of the semiaxes of the molecular (prolate) ellipsoid one calculates $D_{\parallel}/D_{\perp} \approx 1.2$. Only with the unreasonably small ratio $b/a \approx 0.15$, i.e. an extremely cigar-shaped molecule, one obtains a figure $D_{\parallel}/D_{\perp} \approx 10$, as found experimentally in acetonitrile. This model contains 'stick' boundary conditions, with 'slip' conditions (Hu and Zwanzig 1974) the ratio of the diffusion constants becomes $D_{\parallel}/D_{\perp} \rightarrow \infty$. Obviously models based on the shape alone explain $D_{\parallel} > D_{\perp}$ but both models are quantitatively insufficient.

Motional anisotropy was found for nitromethane, $D_{\parallel}/D_{\perp} \approx 9$ (Suchanski and Canepa 1979). The present authors denote $D_{\parallel}$ as 'internal rotational diffusion constant D_i '. In dimethylmercury(II) Lassigne and Wells (1977a) found the large anisotropy $D_{\parallel}/D_{\perp} \approx 40$. This ratio can increase even more if the methyl group is an internally rotating group in a larger molecule. To quote an example, Brown *et al* (1977) report $D_{\parallel}/D_{\perp} \approx 120$ for methylacetatomercury(II).

CH_3Br was investigated by Lassigne and Wells (1977b). $D_{\perp}$ was estimated from dielectric relaxation data,

and consequently from ^2H relaxation rates $D_{\parallel}$ could be calculated. At 25°C the reorientation about the figure axis is about eight times faster than the reorientation of the axis. The temperature dependence of $D_{\perp}$ was approximated by the temperature dependence of D_{μ} calculated from a hydrodynamic approach (Gillen and Noggle 1970),

$$D_{\perp} \approx D_{\mu} = 115 \cdot 10^8 \frac{Td}{\eta M}, \quad (86)$$

where M is the molecular mass, η the viscosity and d the density. With these results from the ^2H relaxation rates, $E_a(D_{\parallel})$ could be calculated. This approximate evaluation procedure has been applied to many studies of symmetric molecules. Wallach and Huntress (1969), Huntress (1970) and Gillen and Noggle (1970) have proposed a quantitative test for whether the small angular step diffusion model may be valid: the ratio

$$\chi = \frac{\tau_{\text{eff}}}{\tau_{FR}}, \quad (87)$$

should be larger than 5; τ_{FR} is the correlation time for free inertial behaviour. The result $\chi_{\parallel} \approx 1-2$, found for CH_3Br and in other studies of symmetric molecules mentioned here, reveals that the absolute figures of $D_{\parallel}$ should be regarded with caution.

CH_3I has been treated earlier with the identical evaluation procedure (Gillen *et al* 1971). Anisotropic reorientation and likewise different activation energies for parallel and perpendicular motion were found. The authors pointed out that the similarity of motional anisotropy in CH_3I and CH_3CN is not surprising because of similar shapes and moments of inertia of the two compounds.

Trihalomethanes CHX_3 , $\text{X} = \text{F}, \text{Cl}, \text{Br}$ have been investigated. In fluoroform the comparison of correlation times from ^2H quadrupolar and ^1H - ^{19}F intramolecular dipolar relaxation rates revealed approximately isotropic reorientation (Chaffin III and Hubbard 1967; Harrel 1976). The anisotropic motion of chloroform has been studied in the neat liquid by Huntress (1969). Although inertial effects were important, ^2H and ^{35}Cl relaxation rates were evaluated with the diffusion model, $D_{\parallel} = 18 \cdot 10^{10} \text{ sec}^{-1}$ and $D_{\perp} = 9.6 \cdot 10^{10} \text{ sec}^{-1}$ at 20°C . The conclusion that anisotropy exists is supported by different activation energies for the two motional modes. Briguet *et al* (1977) investigated 0.05 m solutions of $^{12}\text{CHCl}_3$ and $^{13}\text{CHCl}_3$ in CS_2 . At 30°C they found $D_{\parallel} = 20.9 \cdot 10^{10} \text{ sec}^{-1}$ and $D_{\perp} = 15 \cdot 10^{10} \text{ sec}^{-1}$. With decreasing concentration of electric dipole moments the motion becomes more isotropic but $\chi < 2$ for $\parallel$ and $\perp$ motion emphasizes the importance of inertial effects. Free rotor correlation times for chloroform in the gas phase lead to the result that the perpendicular motion is faster than the C_3 motion. The reverse situation in the liquid is probably caused by 'closer packing' and by self-association through hydrogen bonding along the C_3 axis' (Huntress 1970). In binary systems with benzene (Huntress 1969), with ethers (Eckert *et al* 1974; Helm and Kratochwill 1978) and with hexamethylphosphoramide (Briguet *et al* 1978) an increase of the ratio $D_{\parallel}/D_{\perp}$, as compared with the pure liquid, was observed. The reorientation of the C_3 axis (tumbling motion) is hindered relative to the situation in pure chloroform; hetero-association *via* hydrogen bonds may neatly explain this slowing down of motion. Support comes from the observed increase of the activation energies in the mixture with benzene—a larger increase for the tumbling motion than

CCl_3CN ($\mu \approx 2D$). Their evaluation procedure has been described above (see CH_3Br). BCl_3 and VOCl_3 are two borderline cases concerning the application of diffusional models: in BCl_3 $D_{\parallel}$ and $D_{\perp}$ are in the inertial limit, and the anisotropy $D_{\parallel}/D_{\perp} = \tau_{\perp}/\tau_{\parallel} = 0.75$ agrees well with the ratio of the moments of inertia $(I_{\perp}/I_{\parallel})^{1/2} = 0.71$. In VOCl_3 both motions are in the diffusional limit. Since in most other studies $D_{\parallel}$ is in the inertial and $D_{\perp}$ in the diffusional limit VOCl_3 can be considered as a singular case for the correct quantitative application of the diffusion model. The authors presented a general discussion of rotational motion of spherical top molecules and they arrived at the conclusion that dipole forces were more important than steric or inertial factors in determining motional anisotropy. Recently Chandler (1973, 1978) has argued that the repulsive part of the intermolecular potential is dominant. Indeed all results for symmetric top molecules can be explained on the basis of molecular shape alone. An indication of the importance of attractive forces for molecules with a large dipole moment has been given by Pedersen *et al* (1978), see below. Beyond any doubt hydrogen bonding on the other hand provides a source of motional anisotropy.

Sandhu studied CD_2Cl_2 (1978), CD_2Br_2 (1977) and CD_2I_2 (Sandhu and Peemoeller 1976). In these molecules the dipole axis coincides with the symmetry axis (C_2). Assuming fastest reorientation about this axis a symmetric model may be justified. Sandhu measured ^2H relaxation rates and calculated $D_{\perp}$ from hydrodynamic equations (this procedure has been described above, see (86)). As a result, the (assumed) fast reorientation about the C_2 axis was always verified, $D_{\parallel}/D_{\perp} \approx 4$ (CD_2Cl_2), ≈ 6 (CD_2Br_2), and ≈ 7 (CD_2I_2). The activation energies for $\parallel$ and $\perp$ motion are nearly equal, $E_a(D_{\perp})/E_a(D_{\parallel}) = 1.01$ (CD_2Cl_2), $= 1.07$ (CD_2Br_2), and $= 1.00$ (CD_2I_2). The absolute values increase with increasing size of the substituent X , $E_a(D_{\parallel}) = 8.07$ (CD_2Cl_2), $= 8.73$ (CD_2Br_2), and $= 12.96$ (CD_2I_2) kJ mol^{-1} . The $\parallel$ motion is inertial, $\chi \sim 0.5 - 2$. Because of the multitude of approximations (hydrodynamic model and symmetric model for an asymmetric tumbler) we have only the qualitative result that the motion is more isotropic when the size of the substituent increases; molecular shape is sufficient to rationalize these findings. Mayne *et al* (1976) studied coupled spin relaxation of $^{13}\text{CH}_2\text{I}_2$ dissolved in benzene- d_6 (34 Wt %). The reorientation which involves the least displacement of the bulky iodines was found to be fastest; the ratios $D_{zz}/D_{xx} = 4.9$ and $D_{zz}/D_{yy} = 12.7$ when compared with Sandhu's result, $D_{\parallel}/D_{\perp} \approx 7$, reveal that the symmetric model is indeed an oversimplification.

We discuss now relaxation studies of planar aromatic molecules. The exact evaluation has to be done using the model of an asymmetric tumbler; expressions for the effective correlation times as a function of the rotational diffusion constants have been given in table 3. An approximate analysis can be based on the symmetric model and we have demonstrated in figure 16 that the qualitative conclusions remain valid even if the assumed equality of one in-plane and the out-of-plane rotational diffusion constant is not fulfilled. The influence of shape as well as of intermolecular interactions upon motional anisotropy have been investigated.

Levy *et al* (1973) studied ^{13}C relaxation rates of monosubstituted benzenes. The ratio ρ of (*o*, *m*) and (*p*)-carbon relaxation rates, see (83), provides a qualitative measure of motional anisotropy. We prefer this viewpoint instead of giving a quantitative evaluation in terms of the symmetric model (with $D_{\parallel}$ and $D_{\perp}$). Monosubstituted

benzenes C_6H_5X show a ratio $\rho < 1$ which is consistent with a hindered rotational motion of the C_2 symmetry axis compared with a motion about this axis. Inertial effects (lower momentum of inertia around the C-X bond axis) and steric repulsions (by a motion around the C-X axis fewer surrounding molecules have to be 'pushed away') can explain the experimental result. The anisotropy of motion increases with increasing size of the substituent X; we quote some examples: $X = CH_3$, $\rho = 0.73$; $X = NO_2$, $\rho = 0.70$; $X = CCH$, $\rho = 0.60$; $X = C(CH_3)_3$, $\rho = 0.55$; $X = C_6H_5$, $\rho = 0.54$.

The influence of intermolecular hydrogen bonding has been studied by analogous procedures (Levy 1972; Levy *et al* 1973). ^{13}C relaxation rates of phenol evidence anisotropic motion in concentrated solutions in CCl_4 , $\rho = 0.58$, the reorientation of phenol becomes more isotropic on dilution, $\rho = 0.77$ in an 4 mol % solution in CCl_4 . Linear aggregates are assumed for self-associated phenol which break up at higher dilution. Possibly specific solvent effects are present in an 1:1 mixture of phenol and acetone, $\rho = 0.90$ may indicate 'folded complexes'. Slightly anisotropic tumbling is observed for aniline in carbontetrachloride and dimethylsulphoxide, $\rho = 0.77$ and 0.90. In acidic solution ρ decreases markedly, $\rho = 0.35$ in CH_3CO_2H and $\rho = 0.23$ in CF_3CO_2H (20 vol % solutions). A motion where the anilinium ion is 'locked' in the solvent lattice by ion pairing or electrostatic interactions has been proposed. The self-association *via* carboxyl groups has its counterpart in the motional anisotropy of benzoic acid where long-lived linear dimers may be formed, $\rho = 0.5$ and the non-associated methylbenzoate, $\rho = 0.8$; both 1 M solutions in $(CDCl_3)_2$ at 30°C (Levy and Terpstra 1976).

Pyridine has been shown to be a convenient motional probe for studying hetero-association with hydrogen donor molecules. Campbell *et al* (1975) investigated 1/1 mixtures with monohydric alcohols. The authors observed a monotonous decrease of ρ with increasing size of the alcohol, for example $\rho = 0.76$ (methanol), $\rho = 0.60$ (*n*-pentanol), and $\rho = 0.53$ (*n*-decanol). Kratochwill (1978) has studied the system pyridine-methanol in the concentration range pure pyridine to 10 mol % solutions. The ratio ρ decreases with increasing methanol concentration. Assuming a simple one-step equilibrium, $A + B \rightarrow AB$, an anisotropy ratio $D_{||}/D_{\perp} \approx 4$ for the complexed state AB was found. The AB hetero association leads to a motional anisotropy of the same magnitude as observed for monosubstituted benzenes with a large substituent, *e.g.* C_6H_5 . This may be explained by a methanol-pyridine complex which is stable within the time range of rotational correlation times (psec). Similar specific interactions were detected in binary systems of pyridine and water; the slowest motion is the reorientation of the C_{para} -N axis (Goldammer *et al* 1974; Kintzinger 1975).

We proceed now to a discussion of experiments in which the (full) motional anisotropy of planar rings was determined, mainly by combining ^{13}C relaxation rates with the relaxation rate of one quadrupolar nucleus with a large asymmetry parameter of the quadrupole coupling tensor (Huntress 1970). Some of the results were obtained by using ^{13}C relaxation rates and light-scattering data (Bauer *et al* 1974).

In benzene we have isotropy of motion with respect to the molecular plane (by symmetry) but the rotation about the sixfold axis is about 3.5 times faster than about

combination of ^1C and ^{15}N relaxation rates—Pedersen *et al* (1978) studied pyridine and pyridazine. See figure 18 for structural formulas and orientation of tensor. The motional behaviour of pyridine ($\mu = 2.22\text{ D}$), pyridine ($\mu = 2.33\text{ D}$) and s-triazine ($\mu = 0$) is similar; an anisotropy $D_{\parallel}/D_{\perp} > 1$ (or $D_{zz}/D_{yy,xx}$) was found at low temperatures and the motion becomes more isotropic with increasing temperature. Repulsive forces dominate and dipolar forces can only be verified by comparison with motions which are sterically unhindered. For example the $\parallel$ motion is slightly hindered in pyrimidine and pyridine ($\mu \neq 0$) than in triazine and benzene ($\mu = 0$). Pyridazine ($\mu = 4.22\text{ D}$) shows evidence of the importance of dipolar forces.

The evaluation of motional anisotropy is strongly dependent on a proper choice of the ^{14}N quadrupole coupling constant and the asymmetry parameter. To illustrate some experimental problems we mention the results for pyridine: the figure $D_{\parallel}/D_{\perp}$ at -20°C (Kintzinger and Lehn 1971) has been reevaluated to $D_{\parallel}/D_{\perp} \approx 1.4$ (Schäfer and Spieß 1974; Spieß 1978a)—based on a new value of the quadrupole coupling constant and on CSA (chemical shift anisotropy) relaxation rates ^{15}N . Isotropic correlation with respect to the ring plane is revealed by equal relaxation rates for all components (Goldammer *et al* 1974); Spieß's result—approximately overall isotropic reorientation—may indicate specific interactions in pyridine (dipolar ?) not present in benzene.

Further information comes from the temperature dependence of the rotational and diffusion coefficients evaluated with the absolute rate equation

$$D_{ii} = \frac{kT}{h} \exp\left(\frac{\Delta S_i^{\ddagger}}{R} - \frac{\Delta H_i^{\ddagger}}{RT}\right), \text{ or } \begin{matrix} i = x, y, z \\ i = \parallel, \perp \end{matrix}$$

The activation enthalpies for $D_{\perp}$ (or D_{xx} and D_{yy}) are similar for pyridine, pyridazine and s-triazine, $\approx 10\text{ kJ mol}^{-1}$, and are ≈ 6 times larger than $\Delta H^{\ddagger}(D_{\parallel})$; activation entropies $\Delta S^{\ddagger}(D_{\perp})$, or $\Delta S^{\ddagger}(D_{xx}, D_{yy})$ respectively, are zero within experimental error, supporting the concept that steric interactions dominate. $\Delta S^{\ddagger}(D_{\parallel})$ has a large negative value, $-30\text{ J mol}^{-1}\text{ K}^{-1}$; for free inertial behaviour one calculates $\Delta S^{\ddagger} = -30.1\text{ J mol}^{-1}\text{ K}^{-1}$ (Pedersen *et al* 1978). Activation enthalpies $\Delta H^{\ddagger}(D_{xx}, D_{yy})$ for pyridazine are smaller, 6.3 and 9.2 kJ mol^{-1} , and the $\parallel$ motion is thermally activated, $\Delta H^{\ddagger}(D_{zz}) = 9.2\text{ kJ mol}^{-1}$. Activation entropies are large for $\perp$ motions, $\Delta S^{\ddagger}(D_{xx}) = 25$; $\Delta S^{\ddagger}(D_{yy}) = 15\text{ J mol}^{-1}\text{ K}^{-1}$ and vanish for the $\parallel$ motion, $\Delta S^{\ddagger}(D_{zz}) = 0$. Attractive forces between electric dipoles lead to a strong self-association, for example the stacking of molecules with antiparallel dipoles and thereby a hindered inertial spinning motion (D_{zz}).

Stark *et al* (1977) investigated ^{13}C and ^{14}N relaxation of neat nitrobenzene and 50 vol % solutions of nitrobenzene in eight solvents. In their evaluation procedure

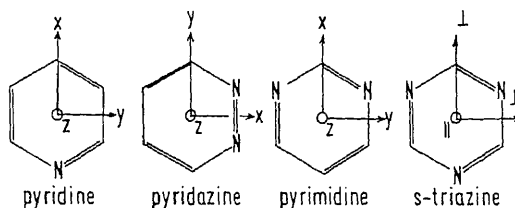


Figure 18. Structural formulas of azabenzene and orientation of diffusion tensor.

vibrationally averaged bond distance $\langle r_{\text{CH}}^{-3} \rangle^{-1/3} = 1.107 \text{ \AA}$ was used and the orientation of the principal axis system of the quadrupole coupling tensor, (asymmetry parameter = 0.404) with respect to the molecule fixed rotational diffusion tensor, was determined by seeking a physically acceptable viscosity dependence of the calculated diffusion constants. The results were in quantitative disagreement with figures given by Bauer *et al* (1974) and Alms *et al* (1973), where ^{13}C relaxation rates have been combined with results from depolarized Rayleigh scattering. Nevertheless the qualitative conclusions remain identical: D_{yy} is smaller than D_{xx} or D_{zz} since the corresponding motion involves the greatest displacement of surrounding solvent molecules. (The axis system of the diffusion tensor is defined as in figure 15b.) This qualitative feature is also retained in a recent analysis of Stark's measurements using a different ^{14}N quadrupole coupling constant (e^2qQ/h) and asymmetry parameter (Lohmann *et al* 1978). In this work the orientation of the principal axis system of the quadrupole coupling tensor disagrees with that used by Stark and that found for solid nitrobenzene. As we have also seen for pyridine the quantitative application of the method of quadrupolar nuclei in planar systems suffers from the lack of knowledge of precise values of the quadrupole coupling tensor in the liquid.

The analysis of coupled spin relaxation in planar aromatic rings offers a possibility for determination of the full diffusion tensor from dipolar relaxation rates alone. This method proved to be a promising new way avoiding the difficulties concerned with quadrupolar relaxation. For AB_2 proton spin systems the principles of the method have been elaborated in full detail and a possible extension to more difficult spin systems has been demonstrated. The non-exponential recovery of individual lines in a high-resolution ^1H spectrum to their equilibrium values in a non-selective $180^\circ - \tau - 90^\circ$ experiment can be analyzed to obtain individual spectral densities J_{ijkl} (i, j, k, l refer to spin numbering), see (75). This evaluation step is independent of any assumption of a motional model. Matrix elements of tensor operators provide selection rules which spectral densities may be determined with sufficient accuracy. In AB_2 spin systems (even in the AX_2 limit) one autocorrelation spectral density J_{ABAB} and one cross-correlation term $J_{ABAB'}$ are such 'good' spectral densities. The two other spectral densities $J_{ABBB'}$ and $J_{BB'BB'}$ are too strongly dependent on the magnitude of external (not intramolecular dipolar) relaxation contributions, *e.g.* a contribution from the solvent. Two more autocorrelation spectral densities come from the ^{13}C relaxation rates of the C_A and C_B carbons. Only the rotational diffusion model allows formulation of consistent expressions for all individual effective correlation times τ_{ijkl} , and all evaluations performed therefore rely on this model. Quotients $\tau_{ijkl}/\tau_{i'j'k'l'}$ define an allowed range of pairs Δ_+ , Δ_- (see (81) and (82)), and with the absolute value of one autocorrelation term τ_{ijij} the three diffusion constants D_{ii} , $i = x, y, z$ (in the principal axis system) can be calculated.

Vold *et al* (1977) studied tri-substituted benzenes with C_{2v} symmetry. $-\text{OH}$ and OCH_3 groups are treated as effectively symmetric substituents located on the x -axis, see figure 19. The results are listed in table 5. The data could be explained in terms of molecular shape. For example D_{xx} increases—relative to D_{yy} and D_{zz} —when the

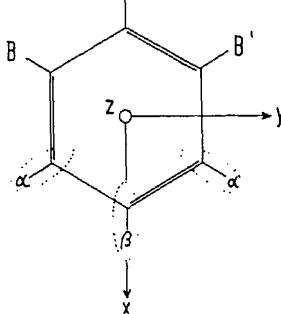


Figure 19. Orientation of the principal diffusional axis system and indexing of nuclei in planar aromatic molecules which provide AB_2 proton spin systems.

Table 5. Rotational diffusion constants of small molecules, in 10^{10} sec^{-1} , obtained by analysis of coupled spin relaxation.

System	D_{xx}	D_{yy}	D_{zz}	References
Trichlorobenzene ^a	2.17 ± 0.06	2.7 ± 0.2	3.8 ± 0.2	Vold <i>et al</i> (1977)
Trichlorobenzene ^b	3.38 ± 0.06	4.5 ± 0.4	5.4 ± 0.1	Vold <i>et al</i> (1977)
Dichloroanisole ^b	3.61 ± 0.06	3.1 ± 0.2	4.4 ± 0.1	Vold <i>et al</i> (1977)
Dichlorophenol ^b	5.4 ± 0.7	2.3 ± 0.7	4.5 ± 0.9	Vold <i>et al</i> (1977)
Dichlorophenol ^c	1.32 ± 0.02	2.84 ± 0.08	2.43 ± 0.19	Kratochwill <i>et al</i> (1979)
Dichlorophenol ^d	1.01 ± 0.05	1.02 ± 0.30	1.52 ± 0.07	Kratochwill <i>et al</i> (1979)
Dichlorophenol ^e	1.12 ± 0.03	0.76 ± 0.30	0.94 ± 0.09	Kratochwill <i>et al</i> (1979)
2-chloropyrimidine ^b	8.8 ± 0.3	1.8 ± 0.8	19.2 ± 1.9	Nery and Canet (1978)
<i>o</i> -Dichlorobenzene ^f	4.9 ± 1.3	3.1 ± 0.9	8.8 ± 0.1	Stark <i>et al</i> (1978)

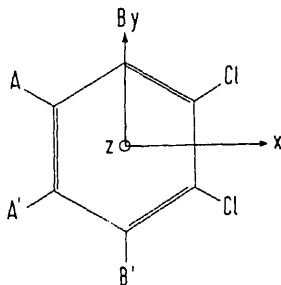
The orientation of the principal axis system is shown in figures 19 and 20; ^a0.1 M in CDCl_3 , 24°C; ^b0.1 M in CS_2 , 24°C; ^c0.1 M in CCl_4 , 22°C; ^d0.1 M in CCl_4 , + 0.1 M added pyridine, 22°C; ^e0.1 M in CCl_4 , + 0.5 M added pyridine, 22°C; ^f0.07 M in CS_2 , 25°C.

closely the ratio of the viscosities (trichlorobenzene in CDCl_3 and in CS_2). The assumption of Gillen and Noggle (1970) that motions which reorient an electric dipole should be slower than those which cannot be confirmed by these data. In contrast to this 'guideline', in trichlorobenzene ($\mu \approx 3.4 \text{ D}$) $D_{yy} > D_{xx}$, but only the motion about y reorients the electric dipole.

Nery and Canet (1978) investigated 0.1 M solutions of 2-chloropyrimidine in CS_2 . They found strongly anisotropic reorientation, $D_{zz} > D_{xx} > D_{yy}$. $\chi_{zz} = 1$ shows that the motion around the z axis is determined by inertial effects, as for triazine (Kintzinger and Lehn 1974) and benzene (Gillen and Griffiths 1972). The authors attribute the large anisotropy of motion to 'specific effects of the two nitrogens'. Previous work of Bovee (1975) showed nearly isotropic reorientation of 2-aminopyridine in an acetone- d_6 - D_2O mixture. This may be ascribed to friction forces between D_2O and 2-aminopyridine (Nery and Canet 1978) but can also artificially result from an approximate data treatment, *e.g.* neglecting intermolecular contributions from the deuterons of the solvent (Vold and Vold 1978). We have hinted above at the importance of a careful analysis of the 'external contributions'.

Stark *et al* (Stark *et al* 1979) extended the technical procedure of coupled spin relaxation to an $AA'BB'$ spin system in their study of *o*-dichlorobenzene. A comparison of the results for *o*-dichlorobenzene (ODCB) with the results for 1,2,3-trichlorobenzene (TCB) reveals the importance of steric effects for D_{xx} and D_{yy} . $D_{xx}(\text{ODCB}) > D_{xx}(\text{TCB})$ because the bulky chlorines are closer to the axis of rotation in ODCB, compare figures 19 and 20, $D_{yy}(\text{ODCB}) \approx D_{yy}(\text{TCB})$ since both motions have to reorient the chlorines. The differences in D_{zz} , or $\tau_z = 1/6 D_{zz}$ respectively, were rationalized in part by inertial effects $I_{zz}(\text{ODCB}) = 1.062 \cdot 10^{-37} \text{ g cm}^2$, $I_{zz}(\text{TCB}) = 1.588 \cdot 10^{-37} \text{ g cm}^2$, and $\tau_i \approx I_{ii}^{1/2}$ for free inertial behaviour.

The influence of intermolecular hydrogen bonding upon molecular reorientation was studied in the system 2,6-dichlorophenol/pyridine (Kratochwill *et al* 1979). 0.1 M solutions of 2,6-dichlorophenol (DCP) in CCl_4 were studied in ternary systems where the acceptor pyridine was added in the ratio 1:1 and 1:5, DCP:pyridine. Due to nearly equal viscosities of pyridine and CCl_4 the acceptor concentration can be varied without changing the macroscopic viscosity. An observed variation of the rotational diffusion constants of DCP with increasing pyridine concentration can therefore safely be ascribed to a direct structural effect and not to a 'background effect' (Grüner and Hertz 1972; Hertz *et al* 1976). ^{13}C relaxation rates of pyridine can in addition be used to study the anisotropy of the motion of pyridine with respect to the ring plane. This provides a qualitative consistency check: intermolecular hydrogen bonding should influence the motional behaviour of both components. Compared with a 0.1 M solution of DCP in CS_2 the rotational diffusion constants in the CCl_4 solution are smaller as can be expected from the ratio of the viscosities. On addition of pyridine D_{yy} and D_{zz} decrease monotonously with increasing acceptor concentration but D_{xx} exhibits only a small variation. Intermolecular association slows down all the above reorientational motions of DCP around axes perpendicular to the axis of the hydrogen bond. Likewise for pyridine the expected anisotropy was found: compared with $\rho \approx 1$ in pure pyridine (Py) it is $\rho = 0.54$ (DCP:Py 1:5) and $\rho = 0.41$ (DCP:Py = 1:1). The decreasing ratio ρ indicates motional anisotropy $D_{xx}/D_{yy} > 1$, i.e. faster reorientation about the axis of the intermolecular hydrogen bond. In model systems where DCP was substituted by 1,2,3-trichlorobenzene and where intermolecular hydrogen bonding is excluded ρ for pyridine remains essentially 1. Intermolecular hydrogen bonding constitutes a strongly anisotropic intermolecular potential and leads to a characteristic variation of motional anisotropy. In the complex a relatively free reorientation about the hydrogen bond axis is preserved and a completely rigid DCP-pyridine complex with a lifetime τ_{eff} can be ruled out.



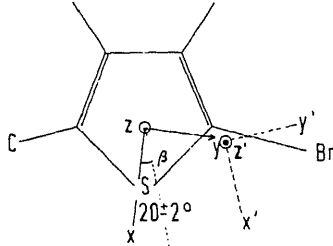


Figure 21. Orientation of the principal axis system of the momentum of inertia tensor (---) and of the rotational diffusion tensor (—) in 2-bromothiophene; ● center of mass.

Anisotropic motion with respect to the ring plane, $D_{yy}/D_{xx} = 2.0 \pm 0.2$ and the orientation of the diffusional tensor, 20° shifted relative to the principal inertial system, could be determined for 2-bromothiophene (Kratohwill and Vold 1980). The *ABC* spin system proved to be unfavourable in a technical sense because only autocorrelation terms are 'good' spectral densities. Approximate figures for cross-correlation terms give an upper limit, $D_{zz} \leq 1 \cdot 10^{11} \text{ sec}^{-1}$. The authors showed that vibrationally averaged internuclear distances must be used in the analysis of ^{13}C relaxation rates. As figure 21 demonstrates the principal axis system is shifted into a direction where the rotation about the *y* axis has minimum steric hindrance in the condensed phase (the *z* axis is determined by symmetry). This shift is also towards the easy axis for electric dipole reorientation comparable to the axis shift found in *N,N*-dimethylformamide (Wallach and Huntress 1969). The anisotropy $D_{yy}/D_{xx} = 2$ is not surprising in view of steric hindrance. The determination of such an axis shift can provide information about the symmetry of the intermolecular potential. D_r is a symmetric tensor in an isotropic liquid and can always be diagonalized (confusing statements are found in the literature), but the principal axis system has not to coincide with the principal axis system that diagonalizes the momentum of inertial tensor!

Summarizing we see that in systems without hydrogen bonding the repulsive part of the intermolecular potential dominates. The influence of electric dipole or dispersive forces can only be detected in sterically unhindered motions. Hydrogen-bonding on the other hand constitutes a source of motional anisotropy: motions which retain the favourable geometry for hydrogen bonds are slightly influenced by this attractive force. The corresponding rotational diffusion constants change only slightly on association. Rotational diffusion constants about axes perpendicular to the direction of the hydrogen bond normally show a decrease on association, the corresponding motions are slowed down.

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Intermolecular light scattering

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1. Introduction

The theoretical foundations of molecular light scattering are due to the insight of Lord Rayleigh, Smoluchowski and Einstein. The subject has since been dealt with in a number of monographs (Cabannes 1929; Born 1933; Fabelinskii 1968; Crosignani *et al* 1975; Berne and Pecora 1976; Long 1977; Kielich 1981). The scientific relevance of elastic light scattering resides in the ease with which it permits the elucidation of the molecular-statistical structure of matter.

1.1 *Studies of integral light scattering*

As predicted by Lord Rayleigh, light scattering by gases and rarefied systems is a source of information regarding the electronic structure of the individual atoms and molecules. The fundamental results of Smoluchowski (1908) and Einstein (1910) have disclosed the stochastic mechanisms of light scattering consisting of spontaneous fluctuations in number density or concentration as well as those of other thermodynamical properties. The fluctuations are generally isotropic in nature; hence, the light scattering process too is isotropic, conserving not only the frequency of the incident light wave, but also its state of polarisation.

Depolarisation of scattered light is caused essentially by anisotropic fluctuations. According to Born (1933) and Cabannes (1929), such fluctuations are due to intrinsic anisotropy of the optical polarizability of the molecules or, after Yvon (1936, 1937), to anisotropy induced in the polarizability of correlated atoms (see Fixman 1955; Theimer and Paul 1965; Macrakis 1967). In a given thermodynamical state of the substance, the two preceding mechanisms leading to anisotropic light scattering are modified by angular correlations between the molecules (Benoit and Stockmayer 1956; Kielich 1958, 1960a).

According to Yvon (1937), statistical translational fluctuations of the dipolar type modify the polarizability of an atom in a fluid causing it to become a function of the density as the result of two- and three-body radial correlations. In addition to these modifications due to long-range forces (Mazur and Mandel 1956; Linder and Krompholt 1970; Frommhold and Proffitt 1978), one generally has to deal with changes

been recently by Gelbart (1974), Knaap and Lallemand (1975), Tabisz (1979), and Amhold (1981).

When Yvon's theory is extended to molecules having intrinsic optical anisotropy, rotational as well as cross translational-orientational fluctuations have to be taken into account, considerably affecting the depolarisation of scattered light (Kielich 1967a,b, 1968a,b, 1971a,b). In the case of polar molecules, agreement between theory and experiment can be enhanced by taking into consideration angular dispersive, electrostatic and inductional binary and ternary interactions (Kielich 1967, 1968a,b; Kielich *et al* 1972; Kielich and Woźniak 1974; Woźniak and Kielich 1975, 1977).

In recent years, numerous authors have discussed anew the applicability of the dipole approximation of the electric molecular field and its utility for the interpretation of the newest experimental observations of scattered light in dense fluids (Ladanyi 1974; Ladanyi and Keyes 1976, 1977a,b, 1978; Keyes 1979).

Moreover, the scattered light intensity has been studied through its dependence on the local field model (Kielich and Pieczyńska 1970; Burnham *et al* 1975; Sullivan and Kielich 1976; Keyes and Ladanyi 1977; Ladanyi and Keyes 1979; Breuer 1980) and multiple scattering (Frisch and McKenna 1965; Boots *et al* 1975; Gelbart 1979; Keyes *et al* 1979; Hynne 1980).

Undeniably, with regard to atomic gases, the electric-dipole approximation suffices to achieve an acceptable degree of accordance with experiment though *e.g.* for helium considerable discrepancies (Barocchi *et al* 1978) and good agreement (Le Duff 1979) have both been reported. However, this is no longer the case when one deals with molecular substances, and higher multipole contributions from the molecular electric field, causing additional variations of the molecular polarizability, have to be included in the calculations. This has first been done by Bullough (1962) for molecular refraction and by Kielich (1965a,b) for distortional electric polarization and more recently, for light scattering, by Pasmantier *et al* (1976) and Kielich (1980). In general, one cannot neglect the contributions from nonlinear multipole polarizabilities (Kielich 1965b, 1970; Hunt 1980; Hunt K L C, Zilles B A and Bohr J E 1981, private communication).

Studies of spectral light scattering

While the integral intensity studies touched on in the preceding sections dealing with the influence of molecular correlations on the process of light scattering, recent years have witnessed rapid progress in the domain of the spectral distribution of scattered light. Thus, beside intermolecular infrared absorption spectroscopy (Van Kranendonk 1974), a new field of intermolecular scattering spectroscopy has arisen (Van Kranendonk 1980) and become a source of valuable information concerning, in addition to translational and rotational motions of the individual molecules, the dynamics of momentary assemblages of molecules correlated in time and space.

The stochastic foundations of the spectral theory of light scattering are, in fact, those of Van Hove's (1954) and Vineyard's (1958) theory of neutron scattering by atomic lattices (Powles 1973; Copley and Lovesey 1975) extended by Steele and Pecora (1965) to the case of x-ray and slow neutron scattering from fluids composed of non-spherical molecules. Here, the problem consists in the formulation of one-, two- and many-body space-time correlation functions, permitting the determination of the dynamical equations in number density, the stochastic treatment of which is due to

Smoluchowski (1906, 1915) in his kinetic theory of translational Brown motions, and has been extended by Chandrasekhar (1943) and Kac (1959) and, more recently, by Brenner *et al* (1978). Besides the kinetic-microscopic treatment of light scattering (Gabriel 1973), thermodynamical-hydrodynamical approaches also exist (Mountain 1977); the two points of view merge in the general theory of irreversible processes, proposed by Mori (1965).

The detailed studies of Starunov *et al* (1967) as well as Stegeman and Stoicheff (1968), of the fine structure of the lines of light scattered from a laser beam in molecular liquids, have disclosed the presence of a doublet in the depolarized part of the spectrum. Laser spectroscopy has made it possible to carry out precise observations of the doublet in the scattered spectrum in numerous liquids consisting of optically anisotropic molecules. For an extensive discussion of these studies we refer the reader to the monographs by Fabelinskii (1968) and Atakhodzhayev and Tukhvatulin (1981) and the reviews by Fleury and Boon (1973) and Ytarova (1980); also, we refer to the experimental results of Stegeman and Stoicheff (1973), Alms *et al* (1973a, b), Dardy *et al* (1973), Bruining and Clarke (1976), and Fröhlich and Posch (1978).

According to the thermodynamical theory of Leontovich (1941) and Rytov (1957), the occurrence of the Rayleigh wing and its doublet is due to light scattering on fluctuations of anisotropy and on deformations of shearing waves in liquids. Starunov and Fabelinskii (1974) have performed an analysis of the complete structure of the scattered light spectrum on the basis of Rytov's theory (1970), involving two anisotropy relaxation times.

Ben-Reuven and Gershon (1969) have formulated a molecular-statistical spectral theory and have applied it in their description of the depolarisation of the Rayleigh line wing on the microscopic level. Other forms of the theory have been proposed by Anderson and Pecora (1971), Keyes and Kivelson (1971, 1972) and Gierke (1976). In liquids, rotational molecular motion is dependent on correlations between the molecules and, in accordance with the Keyes-Kivelson theory, the reorientational relaxation time in the presence of binary correlations, τ_c , is related to the uncorrelated single-particle reorientational time τ_s , as follows:

$$\frac{\tau_c}{\tau_s} = \frac{1 + fN}{1 + gN},$$

where f and g are, respectively, the static and dynamic pair orientational correlations parameters. The above relationship is the subject of numerous studies (Bauer *et al* 1974, 1975; Patterson and Griffiths 1975; Wang *et al* 1976; Cheung *et al* 1976; Rouch *et al* 1976; Jones and Wang 1977; Alms and Patterson 1978; Higashigaki *et al* 1978; Perrot *et al* 1978; Lund *et al* 1979; Hilbert *et al* 1979; Cox *et al* 1979).

The effect of molecular fields on the spectral distribution has also been discussed (Hellwarth 1970; Keyes *et al* 1971; Keyes and Ladanyi 1977; Bancewicz 1979), as well as that of angular correlations (Knast and Kielich 1979; Głaz 1981) and other mechanisms (Bucaro and Litovitz 1971; Van Konynenburg and Steele 1972; Dill *et al* 1975; Rosenthal and Strauss 1976; Bancewicz and Kielich 1981).

dd *et al* 1980; Varshneya *et al* 1981), and in liquid mixtures (Tabisz *et al* 1972; kerson and Hanley 1980).

Outline of the present review

above is ample evidence that theoretical and experimental work on light scattering atomic and molecular media proceeds untiringly and that the number of papers and communications on its various aspects is increasing. Since some results are still theoretically and experimentally controversial, there is an urgent need for a comprehensive, general theory of light scattering well suited to concrete situations in which various molecular correlations are apparent. Accordingly, we shall attempt to propose a uniform though rather formal approach to the foundations of integral and spectral scattering theory. To insure generality and compactness of the mathematics, we shall essentially make use of Cartesian tensor formalism in the approach initiated by Jansen (1958) in his theory of electrostatic multipole interactions and extended by others (Kielich 1965a-f, 1966a, b; De Groot 1969; Stogryn 1971, 1972).

Similarly, as in the complete electromagnetic theory of the refractive index (Vezzetti and Keller 1967; Kielich 1965c, 1966a) and optical activity (Kielich 1975), we consider in general, multipolar electric and magnetic scattering processes separating the intensities into irreducible isotropic, antisymmetric and anisotropic parts. With this aim, we give a systematically developed theory of interactions between electric and magnetic multipoles and external as well as internal electromagnetic fields. This enables us to determine generally the changes in multipolar electric and magnetic polarizabilities of molecules induced by space- and time-fluctuations of the multipole fields. These changes, resulting in general from many-body correlations, are determined by the perturbation method. The procedure outlined permits the calculation of pure contributions of the type 00, 11, 22, 33 etc. and, moreover, of cross contributions 01, 02 and so forth to the scattered light intensity. Especially relevant to antisymmetric scattering are the mixed electro-magnetic and magneto-electric multipolar polarizabilities. In addition to this direct influence of molecular correlations, light scattering is indirectly dependent on them by way of the statistical distribution function, permitting the determination of the mean scattered intensity. These indirect temperature-dependent contributions are calculated by thermodynamical perturbation calculus. The results are expressed in a notation applicable to systems of N like, as well as N unlike scattering centres.

Interaction of electric and magnetic multipoles with electromagnetic field

We consider an assembly of N interacting microsystems (atoms, molecules or ions) subjected to an electromagnetic field with electric and magnetic vectors at the position $\mathbf{r}$ and time t :

$$\mathbf{E}(\mathbf{r}, t) = -\frac{1}{c} \frac{\partial}{\partial t} \mathbf{A}(\mathbf{r}, t) - \nabla \Phi(\mathbf{r}, t),$$

$$\mathbf{H}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t), \quad (1)$$

where $\Phi(\mathbf{r}, t)$ and $\mathbf{A}(\mathbf{r}, t)$ are the scalar and vector potentials at the space-time point $(\mathbf{r}, t)$ and ∇ is the destination operator.

Let the i th microsystem consist of n_i point particles (nuclei and electrons) with electric charges e_{si} , masses m_{si} and positional vectors $\mathbf{R}_{si}$ ($s = 1, 2, \dots, n_i$, $i = 1, 2, \dots, N$). For convenience, we introduce the set of independent coordinates

$$\mathbf{r}_i = \sum_s m_{si} \mathbf{R}_{si} / \sum_s m_{si} \quad \text{and} \quad \mathbf{r}_{si} = \mathbf{R}_{si} - \mathbf{r}_i, \quad (2)$$

where $\mathbf{r}_{si}$ is the (relative) position vector of the s th particle with respect to the center of mass of the microsystem i whose position is $\mathbf{r}_i$ (figure 1).

The Hamiltonian of the spinless microsystem i , in the nonrelativistic classical case, is (Heitler 1954):

$$H_i = \sum_{s=1}^{n_i} \left\{ e_{si} \Phi(\mathbf{R}_{si}, t) + \frac{1}{2c^2 m_{si}} [c \mathbf{p}_{si} - e_{si} \mathbf{A}(\mathbf{R}_{si}, t)]^2 \right\}, \quad (3)$$

in which $\mathbf{p}_{si}$ is the generalized momentum operator of the s th particle of the microsystem i .

The total Hamiltonian of an assembly of N microsystems is

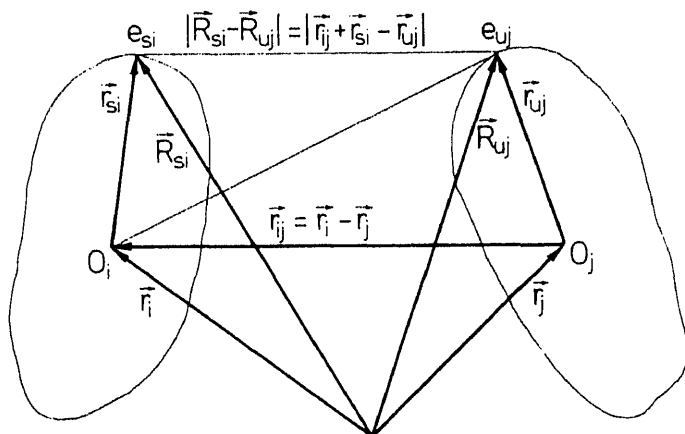
$$HN = \sum_{i=1}^N H_i. \quad (4)$$

The Hamiltonian (3) can, in the well known manner, be resolved into a nonperturbed part $H_i^{(0)}$ and perturbed Hamiltonians of the first and second order of the form

$$H_i^{(1)} = -\frac{1}{2c} \sum_{s=1}^{n_i} \frac{e_{si}}{m_{si}} [\mathbf{p}_{si} \cdot \mathbf{A}(\mathbf{R}_{si}, t) + \mathbf{A}(\mathbf{R}_{si}, t) \cdot \mathbf{p}_{si}] + \sum_{s=1}^{n_i} e_{si} \Phi(\mathbf{R}_{si}, t), \quad (5)$$

$$H_i^{(2)} = \frac{1}{2c^2} \sum_{s=1}^{n_i} \frac{e_{si}^2}{m_{si}} \mathbf{A}(\mathbf{R}_{si}, t) \cdot \mathbf{A}(\mathbf{R}_{si}, t). \quad (6)$$

In the general case when the scalar and vector potentials are not constant within the region of the microsystem (the field is generally nonhomogeneous throughout



of $\vec{r}_{si}$ ($|\vec{r}_{si}| \ll |\vec{r}_i|$):

$$\begin{aligned}\Phi(\mathbf{r}_i + \mathbf{r}_{si}, t) &= \sum_{n=0}^{\infty} \frac{1}{n!} \mathbf{r}_{si}^n [n] \nabla_i^n \Phi(\mathbf{r}_i, t), \\ \mathbf{A}(\mathbf{r}_i + \mathbf{r}_{si}, t) &= \sum_{n=0}^{\infty} \frac{1}{n!} \mathbf{r}_{si}^n [n] \nabla_i^n \mathbf{A}(\mathbf{r}_i, t),\end{aligned}\quad (7)$$

where the symbol $[n]$ in Jansen's (1958) notation denotes n -fold scalar contraction of the product of two n th rank vectors $\mathbf{r}_{si}^n$ and ∇_i^n .

By the expansions (7), the first-order perturbation Hamiltonian (5) can be represented in the form of a multipole expansion (Kielich 1966a):

$$\begin{aligned}H_i^{(1)} &= \sum_{s=1}^{n_i} e_{si} \Phi(\mathbf{r}_i, t) - \sum_{n=0}^{\infty} \frac{1}{(2n-1)!!} \left\{ \mathbf{M}_{ei}^{(n)} [n] \mathbf{E}^{(n)}(\mathbf{r}_i, t) + \right. \\ &\quad \left. + \mathbf{M}_{mi}^{(n)} [n] \mathbf{H}^{(n)}(\mathbf{r}_i, t) \right\},\end{aligned}\quad (8)$$

in which the first term represents the potential energy of the total charge of the microsystem in a scalar potential $\Phi(\mathbf{r}_i, t)$. The second term describes interaction between the 2^n -pole intrinsic electric moment of the microsystem i

$$\mathbf{M}_{ei}^{(n)} = \sum_{s=1}^{n_i} e_{si} r_{si}^n \mathbf{Y}^{(n)}(\mathbf{r}_{si}) \quad (9)$$

and electric field vector of degree n at the point $(\mathbf{r}_i, t)$

$$\mathbf{E}^{(n)}(\mathbf{r}_i, t) = \nabla_i^{n-1} E(\mathbf{r}_i, t). \quad (1a)$$

In the definition (9), $\mathbf{Y}^{(n)}(\mathbf{r})$ is an operator of degree n having the properties of spherical harmonics and determined as follows (Kielich 1965c):

$$\begin{aligned}\mathbf{Y}^{(n)}(\mathbf{r}) &= \frac{1}{n! r^n} \{ (2n-1)!! \mathbf{r}_1 \mathbf{r}_2 \dots \mathbf{r}_n - (2n-3)!! r^2 \sum \mathbf{U}_{12} \mathbf{r}_3 \dots \mathbf{r}_n \\ &\quad + \dots + (-1)^k (2n-2k-1)!! r^{2k} \\ &\quad \sum \mathbf{U}_{12} \dots \mathbf{U}_{2k-1, 2k} \mathbf{r}_{2k+1} \dots \mathbf{r}_n + \dots \} \end{aligned}\quad (10)$$

where $\mathbf{U}_{12}$ denotes the unit tensor of rank two, and $\sum \mathbf{U}_{12} \mathbf{r}_3 \dots \mathbf{r}_n$, etc. are sums of the terms obtained from the one written out by interchanging the suffixes 1, 2, $\dots$ n . The number of terms in the last sum in (10) is equal to $n! / \{2^k (n-2k)! k!\}$.

The third term in the Hamiltonian (8) represents interaction between the 2^n -pole intrinsic magnetic moment of the microsystem i (Kielich 1965c):

$$\mathbf{M}_{mi}^{(n)} = \frac{n}{(n+1)c} \sum_{s=1}^{n_i} e_{si} r_{si}^n \mathbf{Y}^{(n)}(\mathbf{r}_{si}) \times \dot{\mathbf{r}}_{si} \quad (11)$$

and the magnetic field vector of degree n at the point $(\mathbf{r}_i, t)$

$$\mathbf{H}^{(n)}(\mathbf{r}_i, t) = \nabla_i^{n-1} \mathbf{H}(\mathbf{r}_i, t) = \nabla_i^n \times \mathbf{A}(\mathbf{r}_i, t). \quad (1b)$$

With respect to (7), the second-order perturbation Hamiltonian (6) is obtained as follows (Kielich 1965c):

$$\mathbf{H}^{(n_1)}(\mathbf{r}_i, t) [n_1] \mathbf{A}_{mi}^{(n_2)} [n_2] \mathbf{H}^{(n_2)}(\mathbf{r}_i, t), \quad (12)$$

where we have introduced the tensor of rank $n_1 + n_2$

$$\begin{aligned} \mathbf{A}_{mi}^{(n_2)} = & \frac{n_1 n_2}{(n_1 + 1)(n_2 + 1)c^2} \sum_{s=1}^{n_1} \frac{e_{si}}{m_{si}} r_{si}^{n_1+n_2} \{ \mathbf{Y}^{(n_1)}(\mathbf{r}_{si}) \mathbf{Y}^{(n_2)}(\mathbf{r}_{si}) - \\ & - \mathbf{Y}^{(n_1)}(\mathbf{r}_{si}) \cdot \mathbf{Y}^{(n_2)}(\mathbf{r}_{si}) \mathbf{U} \} \end{aligned} \quad (13)$$

determining the multipole (dia) magnetic polarizability operator of the microsystem i .

Our multipole expansion Hamiltonians (8) and (12) obtained by the Cartesian tensor method can be given immediately in spherical tensor representation (Gray 1976; Gray and Stiles 1976).

3. Long-range multipole forces

We shall now discuss the perturbation Hamiltonians (5) and (6) from internal fields existing in an assembly of interacting microsystems. Neglecting retarded time effects, we have for the scalar and vector potentials

$$\begin{aligned} \Phi^{\text{int}}(\mathbf{R}_{si}) &= \sum_{j \neq i}^N \sum_{u=1}^{n_j} \frac{e_{uj}}{|\mathbf{R}_{si} - \mathbf{R}_{uj}|}, \\ \mathbf{A}^{\text{int}}(\mathbf{R}_{si}) &= \frac{1}{c} \sum_{j \neq i}^N \sum_{u=1}^{n_j} \frac{e_{uj} \dot{\mathbf{R}}_{uj}}{|\mathbf{R}_{si} - \mathbf{R}_{uj}|}, \end{aligned} \quad (14)$$

where, by (2) (also see figure 1):

$$|\mathbf{R}_{si} - \mathbf{R}_{uj}| = |\mathbf{r}_{ij} + \mathbf{r}_{si} - \mathbf{r}_{uj}|. \quad (2a)$$

In the special case of nonoverlapping microsystems when $|\mathbf{r}_{si} + \mathbf{r}_{uj}| < |\mathbf{r}_{ij}|$ we can expand (14) in the form of a double Taylor series (Jansen 1958):

$$|\mathbf{R}_{si} - \mathbf{R}_{uj}|^{-1} = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \frac{(-1)^{n_2+1}}{n_1! n_2!} \mathbf{r}_{si}^{n_1} [n_1]^{(n_1)} \mathbf{T}_{ij}^{(n_2)} [n_2] \mathbf{r}_{uj}^{n_2}, \quad (14a)$$

wherein the tensor of rank $n_1 + n_2$

$$\mathbf{T}_{ij}^{(n_2)} = -\nabla_i^{n_1} \nabla_j^{n_2} |\mathbf{r}_{ij}|^{-1} = (-1)^{n_1+n_2} \mathbf{T}_{ji}^{(n_2)} \quad (15)$$

describes $(2^{n_1}\text{-pole}) - (2^{n_2}\text{-pole})$ -type interactions between microsystems i and j distant by $\mathbf{r}_{ij}$.

With regard to (4), (5), (14) and (14a) we obtain for the total first-order perturbation Hamiltonian resulting from internal long-range forces (Kielich 1965c, 1966a):

$$\begin{aligned} H_{\text{int}}^{(1)} = & -\frac{1}{2} \sum_{i=1}^N \left\{ \sum_{n=0}^{\infty} \frac{1}{(2n-1)!!} \mathbf{M}_{ei}^{(n)} [n] \mathbf{F}_{0e}^{(n)}(\mathbf{r}_i) + \right. \\ & \left. + \sum_{n=0}^{\infty} \frac{1}{(2n-1)!!} \mathbf{M}_{mi}^{(n)} [n] \mathbf{F}_{0m}^{(n)}(\mathbf{r}_i) \right\}, \end{aligned} \quad (16)$$

$$\mathbf{F}_{0e}^{(n)}(\mathbf{r}_i) = \sum_{j \neq i}^N \sum_{n_1=1}^{\infty} \frac{(-1)^{n_1}}{(2n_1-1)!!} {}^{(n)}\mathbf{T}_{ij}^{(n_1)}[n_1] \mathbf{M}_{ej}^{(n_1)}. \quad (17)$$

Similarly, the magnetic internal field of degree n at the centre of the microsystem i is (Kielich 1962, 1966a)

$$\mathbf{F}_{0m}^{(n)}(\mathbf{r}_i) = \sum_{j \neq i}^N \sum_{n_1=1}^{\infty} \frac{(-1)^{n_1}}{(2n_1-1)!!} {}^{(n)}\mathbf{T}_{ij}^{(n_1)}[n_1] \mathbf{M}_{mj}^{(n_1)}. \quad (18)$$

On substituting in (16) the fields (17) and (18), we obtain in explicit form the Hamiltonian (Kielich 1966a):

$$H_{\text{int}}^{(1)} = -\frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \frac{(-1)^{n_2}}{(2n_1-1)!! (2n_2-1)!!} \cdot \{ \mathbf{M}_{ei}^{(n_1)}[n_1] {}^{(n_1)}\mathbf{T}_{ij}^{(n_2)}[n_2] \mathbf{M}_{ej}^{(n_2)} + \mathbf{M}_{mi}^{(n_1)}[n_1] {}^{(n_1)}\mathbf{T}_{ij}^{(n_2)}[n_2] \mathbf{M}_{mj}^{(n_2)} \}, \quad (19)$$

where the first term arises from electrostatic interaction between the intrinsic electric multipoles of an assembly of N micro-systems and the second term arises from magnetostatic interaction between the intrinsic magnetic multipoles of the micro-systems (see also Chiu 1979).

In the same way, we obtain expressions for the higher-order intermolecular Hamiltonians (Kielich 1965e; Stogryn 1971, 1972).

The application of these general expressions, such as (19), to concrete special cases is a rather straightforward procedure and the results are given in many papers (see *e.g.* Kielich 1972; Isnard *et al* 1976; Galatry and Gharbi 1980). Tables of non-zero and independent tensor elements of the electric quadrupole, octopole and hexadecapole moments for all point groups have been published by Kielich and Zawodny (1971) (see also Kielich 1972, 1981). Also, the numerical values of these multipoles for various simpler molecules are available (Stogryn and Stogryn 1966; Kielich 1972; Birnbaum and Cohen 1975, 1976; Isnard *et al* 1980; Birnbaum and Sutter 1981).

Expressions for the molecular interaction Hamiltonians in terms of irreducible spherical multipole tensors have been given by Gray (1968), Riera and Meath (1973), Moraal (1976) and Leavitt (1980).

4. Multipole electro-magnetic polarizabilities

4.1 Induced multipole moments of a microsystem

Let us consider a microsystem acted on by the electric and magnetic fields

$$\begin{aligned} \mathbf{E}(\mathbf{r}, t) &= \mathbf{E}(\omega, \mathbf{k}) \exp \{i(\mathbf{k} \cdot \mathbf{r} - \omega t)\} + \text{C.C.}, \\ \mathbf{H}(\mathbf{r}, t) &= \mathbf{H}(\omega, \mathbf{k}) \exp \{i(\mathbf{k} \cdot \mathbf{r} - \omega t)\} + \text{C.C.} \end{aligned} \quad (20)$$

of a monochromatic light wave vibrating with the frequency ω and having the propagation vector $\mathbf{k}$.

eigenfunction $\psi_g(\mathbf{r})$ of the unperturbed Hamiltonian $H^{(0)}$ of the microsystem in the presence of the fields (20) is given by the vector of state $|\psi_g(\mathbf{r}, t)\rangle$, which has to fulfil the Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} |\psi_g(\mathbf{r}, t)\rangle = \{H^{(0)} + H^{(1)} + H^{(2)} + \dots\} |\psi_g(\mathbf{r}, t)\rangle, \quad (21)$$

where the perturbation Hamiltonians of the microsystem are given by (8) and (12).

We express the wave function of the perturbed microsystem $\psi_g(\mathbf{r}, t)$ in terms of the following expansion:

$$\psi_g(\mathbf{r}, t) = \sum_k c_{kg}(t) \psi_k^{(0)}(\mathbf{r}) \exp(-i\omega_k t), \quad (22)$$

where the coefficients for a transition of the microsystem from the quantum state $|g\rangle$ to the state $|k\rangle$ under the influence of the perturbation are functions of time and can be expanded in a series, as follows:

$$c_{kg}(t) = c_{kg}^{(0)}(t) + c_{kg}^{(1)}(t) + c_{kg}^{(2)}(t) + \dots = \sum_{p=0}^{\infty} c_{kg}^{(p)}(t). \quad (22a)$$

The solution of the problem is dependent on the initial conditions assumed, and we write in the zeroth approximation (Louisell 1973)

$$c_{kg}^{(0)}(t) = \delta_{kg} \exp(-\Gamma_k t/2), \quad (22b)$$

since even in the isolated case the levels of the microsystems almost always possess a finite width for various reasons; Γ_k^{-1} is the lifetime of the quantum state $|k\rangle$.

With regard to the initial condition (22b) we obtain, by (21) and (22), the following equation determining the transition coefficients for $p = 1, 2, 3 \dots$ (Pióciniczak 1980):

$$i\hbar \frac{\partial}{\partial t} c_{kg}^{(p)}(t) = -i\hbar (\Gamma_k/2) c_{kg}^{(p)} + \sum_l \{H_{kl}^{(1)}(t) + H_{kl}^{(2)}(t) + \dots\} c_{lg}^{(p-1)}(t) \exp(i\omega_{kl} t), \quad (23)$$

where the matrix elements of the perturbation Hamiltonians $H_{kl}^{(1)}(t), \dots$ are defined as usual.

The form of the equation of motion (23) is consistent with the approach of Orr and Ward (1971).

Now our problem consists in calculating the electric or magnetic multipole moment $\mathbf{M}_{e,m}^{(n)}(t)$ induced in the microsystems by the fields (20). By quantum-mechanical statistics we have

$$\mathbf{M}_{e,m}^{(n)}(\mathbf{r}, t) = \sum_g \rho_g \int \Psi_g^*(\mathbf{r}, t) \mathbf{M}_{e,m}^{(n)} \Psi_g(\mathbf{r}, t) d\tau, \quad (24)$$

where ρ_g is the statistical matrix in the quantum state g .

By the definition (24) and expression (22), the induced electric or magnetic multipole moment can be expanded as follows:

$$\mathbf{M}_{e,m}^{(n)}(\mathbf{r}, t) = \sum_{p=0}^{\infty} \mathbf{M}_{e,m}^{(n)}(\mathbf{r}, t)^{(p)}, \quad (25)$$

$$\mathbf{M}_{e,m}^{(n)}(\mathbf{r}, t)^{(p)} = \sum_{q=0} \sum_{gkl} \rho_g c_{kg}^{(q)}(t)^* \langle k | \mathbf{M}_{e,m}^{(n)} | l \rangle \langle l_g^{(p-q)}(t). \quad (26)$$

Restricting our present considerations to the first-order Hamiltonian (8) with time-dependent fields of the type (20), we obtain from (23):

$$c_{kg}^{(1)}(t) = -\frac{1}{\hbar} \frac{\langle k | H^{(1)}(\omega) | g \rangle}{\omega_{kg} - \omega - i\Gamma_{kg}} \exp[i(\omega_{kg} - \omega + i\Gamma_g/2)t] + \text{C.C.}, \quad (23a)$$

where $H^{(1)}(\omega)$ is the Fourier frequency transform of the Hamiltonian (8) and $\Gamma_{kg} = (\Gamma_k - \Gamma_g)/2$ determines the level widths of the microsystem for the transition $\langle k | \leftarrow | g \rangle$.

By (23a) with (8) we obtain from (26) for the linear (first-order) electric multipole moment of the microsystem (Kielich 1965c, 1975)

$$\begin{aligned} \mathbf{M}_e^{(n)}(\mathbf{r}, t)^{(1)} = & \sum_{n_1=1}^{\infty} \frac{1}{(2n_1-1)!!} \{ {}^{(n)}_e \mathbf{A}_e^{(n_1)}(\omega) [n_1] \mathbf{E}^{(n_1)}(\mathbf{r}, t) + \\ & + {}^{(n)}_e \mathbf{A}_m^{(n_1)}(\omega) [n_1] \mathbf{H}^{(n_1)}(\mathbf{r}, t) \}, \end{aligned} \quad (27)$$

where the tensor of rank $n + n_1$

$$\begin{aligned} {}^{(n)}_e \mathbf{A}_e^{(n_1)}(\omega) = & \frac{1}{\hbar} \sum_{gk} \rho_g \left\{ \frac{\langle g | \mathbf{M}_e^{(n)} | k \rangle \langle k | \mathbf{M}_e^{(n_1)} | g \rangle}{\omega_{kg} - \omega - i\Gamma_{kg}} + \right. \\ & \left. + \frac{\langle g | \mathbf{M}_e^{(n_1)} | k \rangle \langle k | \mathbf{M}_e^{(n)} | g \rangle}{\omega_{kg} + \omega + i\Gamma_{kg}} \right\} \exp(-\Gamma_g t) \end{aligned} \quad (28)$$

defines the linear 2^n -pole electric polarizability induced in the microsystem by 2^{n_1} -pole electric transitions.

Similarly, the tensor ${}^{(n)}_e \mathbf{A}_m^{(n_1)}(\omega)$ determines the linear 2^n -pole electric polarizability induced in the microsystem by 2^{n_1} -pole magnetic transitions and can be obtained immediately from (28) on replacing therein $\mathbf{M}_e^{(n_1)}$ by $\mathbf{M}_m^{(n_1)}$.

On replacing in the expression (27) the index e by m and m by e as well as $\mathbf{E}^{(n_1)}$ by $\mathbf{H}^{(n_1)}$ and vice versa, we obtain automatically the expression for the linear magnetic multipole moment.

4.2 Variations in polarizability tensor due to multipolar fields

Generally, in a condensed system such as a compressed gas or a liquid, even in the absence of external fields (20), molecular multipole fields (17) and (18) exist owing to the presence of intrinsic or induced multipole moments (9) and (11). In the presence of external fields $\mathbf{E}_0(\mathbf{r}, t)$ and $\mathbf{H}_0(\mathbf{r}, t)$, the molecular fields $\mathbf{F}_{0e}(\mathbf{r})$ and $\mathbf{F}_{0m}(\mathbf{r})$ undergo a change as the result of polarization of the microsystems of the medium, and have to be replaced by molecular fields

$$\begin{aligned} \mathbf{F}_e^{(n)}(\mathbf{r}_i, t) = & \sum_{j \neq i}^N \sum_{n_1=1}^{\infty} \frac{(-1)^{n_1}}{(2n_1-1)!!} {}^{(n)} \mathbf{T}_{ij}^{(n_1)}(\omega) [n_1] \mathbf{M}_e^{(n_1)}(\mathbf{r}_j, t), \\ \mathbf{F}_m^{(n)}(\mathbf{r}_i, t) = & \sum_{j \neq i}^N \sum_{n_1=1}^{\infty} \frac{(-1)^{n_1}}{(2n_1-1)!!} {}^{(n)} \mathbf{T}_{ij}^{(n_1)}(\omega) [n_1] \mathbf{M}_m^{(n_1)}(\mathbf{r}_j, t) \end{aligned} \quad (29)$$

which, in general, are functions of $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{H}(\mathbf{r}, t)$.

In (29), the interaction tensor has the form

$${}^{(n_1)}\mathbf{T}_{ij}^{(n_2)}(\omega) = -\nabla_i^{n_1-1} \nabla_j^{n_2-1} \left[\nabla_i \nabla_j - \left(\frac{\omega}{c} \right)^2 \mathbf{U} \right] |\mathbf{r}_{ij}|^{-1} \exp \left(i \frac{\omega}{c} |\mathbf{r}_{ij}| \right), \quad (30)$$

which, for $(\omega/c) |\mathbf{r}_{ij}| \ll 1$, reduces to (15).

Hence, in a condensed medium, each (*e.g.* the i th) microsystem is acted on, in addition to the external fields $\mathbf{E}(\mathbf{r}_i, t)$ and $\mathbf{H}(\mathbf{r}_i, t)$, by the multipole fields (29). Consequently, the total multipole moments of the i th microsystem are now functions of the effective fields $\mathbf{E}_0(\mathbf{r}, t) + \mathbf{F}_e(\mathbf{r}, t)$ and $\mathbf{H}_0(\mathbf{r}, t) + \mathbf{F}_m(\mathbf{r}, t)$. On restricting ourselves to a linear approximation we have by (27) and (29) for the total electric multipole moment of the i th microsystem (neglecting inhomogeneity of the external electric field *i.e.* writing $\mathbf{E}^{(n)} = 0$ for $n \geq 2$ and external magnetic field $\mathbf{H}^{(n)} = 0$):

$$\begin{aligned} \mathbf{M}_e^{(n)}(\mathbf{r}_i, t) = & \mathbf{M}_{0e}^{(n)}(\mathbf{r}_i) + {}^{(n)}_e \mathbf{A}_{ei}^{(1)}(\omega) \cdot \mathbf{E}_0(\mathbf{r}_i, t) + \sum_{n_1=1}^{\infty} \frac{1}{(2n_1-1)!!} \times \\ & \times \{ {}^{(n)}_e \mathbf{A}_{ei}^{(n_1)}(\omega) [n_1] \mathbf{F}_e^{(n_1)}(\mathbf{r}_i, t) + {}^{(n)}_e \mathbf{A}_{mi}^{(n_1)}(\omega) [n_1] \mathbf{F}_m^{(n_1)}(\mathbf{r}_i, t) \}, \end{aligned} \quad (31)$$

where the total multipole electric and magnetic fields are of the form (for simplicity, we have omitted the higher order terms) (Kielich 1965a):

$$\begin{aligned} \mathbf{F}_e^{(n)}(\mathbf{r}_i, t) = & \mathbf{F}_e^{(n)}(\mathbf{r}_i) + \sum_{j \neq i} \sum_{n_1=1}^{\infty} \frac{(-1)^{n_1}}{(2n_1-1)!!} \times \\ & \times {}^{(n)}\mathbf{T}_{ij}^{(n_1)}(\omega) [n_1] {}^{(n_1)}_e \mathbf{A}_{ej}^{(1)}(\omega) \cdot \mathbf{E}(\mathbf{r}_j, t) + \dots \end{aligned} \quad (32)$$

$$\begin{aligned} \mathbf{F}_m^{(n)}(\mathbf{r}_i, t) = & \mathbf{F}_m^{(n)}(\mathbf{r}_i) + \sum_{j \neq i} \sum_{n_1=1}^{\infty} \frac{(-1)^{n_1}}{(2n_1-1)!!} \times \\ & \times {}^{(n)}\mathbf{T}_{ij}^{(n_1)}(\omega) [n_1] {}^{(n_1)}_m \mathbf{A}_{ej}^{(1)}(\omega) \cdot \mathbf{E}(\mathbf{r}_j, t) + \dots \end{aligned} \quad (33)$$

The expressions (31)–(33) lead, for the electric dipole moment induced in the i th microsystem immersed in a dense medium, to

$$\mathbf{M}_e(\mathbf{r}_i, t) = \Pi_{ei}(\omega) \cdot \mathbf{E}_0(\mathbf{r}_i, t), \quad (34)$$

where

$$\Pi_{ei}(\omega) = \Pi_{ei}(\omega)^{(0)} + \Pi_{ei}(\omega)^{(1)} + \Pi_{ei}(\omega)^{(2)} + \dots = \sum_{p=0}^{\infty} \Pi_{ei}(\omega)^{(p)} \quad (35)$$

is the second-rank tensor of linear electric dipole polarizability of the i th microsystem in the presence of fluctuations of the multipolar electric and magnetic fields.

In the zeroth approximation we assume no long-range multipole field to be present, so that the second-rank tensor

$$\Pi_{ei}(\omega)^{(0)} = {}^{(1)}_e \mathbf{A}_{ei}^{(1)}(\omega) \equiv {}_e \mathbf{A}_{ei}(\omega) \quad (35a)$$

represents the linear electric-dipole polarizability of an individual microsystem (one-body contribution).

The successive terms of the expansion (35) determine variations in dipole polarizability of the first, second, . . . etc. order perturbations due to the action of the electric and magnetic multipole fields (many-body interaction contributions). In the first order

$$\begin{aligned}
\Pi_{ei}(\omega)^{(1)} &= \sum_{j \neq i}^N \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{(-1)^{n_2}}{(2n_1-1)!!(2n_2-1)!!} \times \\
&\times \{ {}^{(1)}_e \mathbf{A}_{ei}^{(n_1)}(\omega) [n_1] {}^{(n_1)}\mathbf{T}_{ij}^{(n_2)}(\omega) [n_2] {}^{(n_2)}_e \mathbf{A}_{ej}^{(1)}(\omega) + \\
&+ {}^{(1)}_e \mathbf{A}_{mi}^{(n_1)}(\omega) [n_1] {}^{(n_1)}\mathbf{T}_{ij}^{(n_2)}(\omega) [n_2] {}^{(n_2)}_m \mathbf{A}_{ej}^{(1)}(\omega) \}, \quad (36)
\end{aligned}$$

In the second-order approximation the linear dipole polarizability variations are given by (three-body interactions contribution)

$$\begin{aligned}
\Pi_{ei}(\omega)^{(2)} &= \sum_{j \neq i}^N \sum_{k \neq j}^N \sum_{n_1=1}^{\infty} \cdots \sum_{n_4=1}^{\infty} \frac{(-1)^{n_2+n_4}}{(2n_1-1)!! \cdots (2n_4-1)!!} \times \\
&\times \{ {}^{(1)}_e \mathbf{A}_{ei}^{(n_1)}(\omega) [n_1] {}^{(n_1)}\mathbf{T}_{ij}^{(n_2)}(\omega) [n_2] {}^{(n_2)}_e \mathbf{A}_{ej}^{(n_3)}(\omega) + \\
&+ {}^{(1)}_e \mathbf{A}_{mi}^{(n_1)}(\omega) [n_1] {}^{(n_1)}\mathbf{T}_{ij}^{(n_2)}(\omega) [n_2] {}^{(n_2)}_m \mathbf{A}_{ej}^{(n_3)}(\omega) + \dots \} \\
&\times [n_3] {}^{(n_3)}\mathbf{T}_{jk}^{(n_4)}(\omega) [n_4] {}^{(n_4)}_e \mathbf{A}_{ek}^{(1)}(\omega). \quad (37)
\end{aligned}$$

The perturbation expansion (35) with (36) and (37) in the electric-dipole approximation represents the well-known result of Yvon (1936, 1937) and Kirkwood (1936).

4.3 Contributions from nonlinear multipole polarizabilities

We now consider the further contributions to the effective polarizability (35) from induced dipole moments of the second and third orders given by (26) for $p = 2$ and $p = 3$, respectively. The electric multipole moment resulting from second-order perturbation theory is given, at the frequency ω , by:

$$\begin{aligned}
\mathbf{M}_e^{(n)}(\mathbf{r}_i, t)^{(2)} &= \frac{1}{2} \sum_{n_1=1}^{\infty} \frac{1}{(2n_1-1)!!} \{ {}^{(n)}_e \mathbf{B}_{eei}^{(1+n_1)}(\omega) + \\
&+ {}^{(n)}_e \mathbf{B}_{eei}^{(n_1+1)}(\omega) \} [1+n_1] \mathbf{E}_0(\mathbf{r}_i, t) \mathbf{F}_e^{(n_1)}(\mathbf{r}_i) + \\
&+ \frac{1}{2} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{1}{(2n_1-1)!!(2n_2-1)!!} {}^{(n)}_e \mathbf{B}_{eei}^{(n_1+n_2)}(\omega) [n_1+n_2] \\
&\times \{ \widehat{\mathbf{F}}_e^{(n_1)}(\mathbf{r}_i, t) \mathbf{F}_e^{(n_2)}(\mathbf{r}_i) + \mathbf{F}_e^{(n_1)}(\mathbf{r}_i) \mathbf{F}_e^{(n_2)}(\mathbf{r}_i, t) \}, \quad (38)
\end{aligned}$$

where the $n+n_1+n_2$ -rank tensor ${}^{(n)}_e \mathbf{B}_{eei}^{(n_1+n_2)}(\omega)$ defines the second-order nonlinear 2^n -pole electric polarizability induced in the microsystem by $2^{n_1+n_2}$ -pole electric transitions.

The electric multipole field existing at the centre of the i th microsystem immersed in the medium when the external field is absent is now of the form (Kielich 1965a)

$$\begin{aligned}
\mathbf{F}_e^{(n)}(\mathbf{r}_i) &= \mathbf{F}_{0e}^{(n)}(\mathbf{r}_i) + \sum_{j \neq i}^N \sum_{k \neq j}^N \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \sum_{n_3=1}^{\infty} \times \\
&\times \frac{(-1)^{n_1+n_3}}{(2n_1-1)!!(2n_2-1)!!(2n_3-1)!!} \\
&\times {}^{(n)}\mathbf{T}_{ij}^{(n_1)}[n_1] {}^{(n_1)}_e \mathbf{A}_{ej}^{(n_2)}(\omega) [n_2] {}^{(n_2)}\mathbf{T}_{jk}^{(n_3)}[n_3] \mathbf{M}_e^{(n_3)}(\mathbf{r}_k), \quad (39)
\end{aligned}$$

multipole electric field (17) or multipole electric fields (32) and (17) causes nonlinear multipole polarizabilities which lead to an additional contribution to the linear effective polarizability (35) (Kielich 1965, 1980), namely to the two-body contribution

$$\Pi_{ei}(\omega)_{NL}^{(1)} = \frac{1}{2} \sum_{j \neq i}^N \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{(-1)^{n_2}}{(2n_1-1)!!(2n_2-1)!!} \{ {}^{(1)}\mathbf{B}_{eei}^{(1+n_1)}(\omega) + {}^{(1)}\mathbf{B}_{eei}^{(n_1+1)}(\omega) \} [n_1]^{(n_1)} \mathbf{T}_{ij}^{(n_2)} [n_2] \mathbf{M}_e^{(n_2)}(\mathbf{r}_j), \quad (40a)$$

as well as the three-body contribution

$$\begin{aligned} \Pi_{ei}(\omega)_{NL}^{(2)} = & \frac{1}{2} \sum_{j \neq i}^N \sum_{k \neq j}^N \sum_{n_1=1}^{\infty} \cdots \sum_{n_4=1}^{\infty} \frac{(-1)^{n_2+n_4}}{(2n_1-1)!! \cdots (2n_4-1)!!} \times \\ & \times \{ {}^{(1)}\mathbf{B}_{eei}^{(1+n_1)}(\omega) + {}^{(1)}\mathbf{B}_{eei}^{(n_1+1)}(\omega) \} [n_1]^{(n_1)} \mathbf{T}_{ij}^{(n_2)} [n_2] \times \\ & \times {}^{(n_2)}\mathbf{A}_{ej}^{(n_3)} [n_3] {}^{(n_3)}\mathbf{T}_{jk}^{(n_4)} [n_4] \mathbf{M}_e^{(n_4)}(\mathbf{r}_k) + \\ & + \frac{1}{2} \sum_{j \neq i}^N \sum_{k \neq j}^N \sum_{n_1=1}^{\infty} \cdots \sum_{n_4=1}^{\infty} \frac{(-1)^{n_3+n_4}}{(2n_1-1)!! \cdots (2n_4-1)!!} {}^{(1)}\mathbf{B}_{eei}^{(n_1+n_2)}(\omega) \\ & \times [n_1+n_2] \{ {}^{(n_1)}\mathbf{T}_{ij}^{(n_3)}(\omega) [n_3] {}^{(n_3)}\mathbf{A}_{ej}^{(1)}(\omega) {}^{(n_2)}\mathbf{T}_{jk}^{(n_4)} [n_4] \mathbf{M}_e^{(n_4)}(\mathbf{r}_k) + \\ & + {}^{(n_1)}\mathbf{T}_{ij}^{(n_3)} [n_3] \mathbf{M}_e^{(n_3)}(\mathbf{r}_j) {}^{(n_2)}\mathbf{T}_{jk}^{(n_4)}(\omega) [n_4] {}^{(n_4)}\mathbf{A}_{ek}^{(1)}(\omega) \}. \end{aligned} \quad (40b)$$

Similarly, the expression (26) leads to the third-order electric multipole moment induced at the frequency ω :

$$\begin{aligned} \mathbf{M}_e^{(n)}(\mathbf{r}_i, t)^{(3)} = & \frac{1}{12} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{S(1, n_1, n_2)}{(2n_1-1)!!(2n_2-1)!!} \times \\ & \times {}^{(n)}\mathbf{C}_{eeei}^{(1+n_1+n_2)}(\omega) [1+n_1+n_2] \mathbf{E}_0(\mathbf{r}, t) \mathbf{F}_e^{(n_1)}(\mathbf{r}_i) \mathbf{F}_e^{(n_2)}(\mathbf{r}_i) + \\ & + \frac{1}{12} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \sum_{n_3=1}^{\infty} \frac{S(n_1, n_2, n_3)}{(2n_1-1)!!(2n_2-1)!!(2n_3-1)!!} \times \\ & \times {}^{(n)}\mathbf{C}_{eeei}^{(n_1+n_2+n_3)}(\omega) [n_1+n_2+n_3] \mathbf{F}_e^{(n_1)}(\mathbf{r}_i, t) \mathbf{F}_e^{(n_2)}(\mathbf{r}_i) \mathbf{F}_e^{(n_3)}(\mathbf{r}_i), \end{aligned} \quad (41)$$

where $S(n_1, n_2, n_3, \dots)$ is a symmetrizing operator consisting in summation over all permutations $n_1, n_2, n_3, \dots$.

In (41) the $(n+n_1+n_2+n_3)$ -rank tensor ${}^{(n)}\mathbf{C}_{eeei}^{(n_1+n_2+n_3)}$ describes the third-order nonlinear 2^n -pole electric polarizability produced by $2^{n_1+n_2+n_3}$ -pole electric transitions.

In particular, we obtain by (39) and (41) for the second-order contributions

$$\begin{aligned} \Pi_{ei}(\omega)_{NL}^{(2)} = & \frac{1}{12} \sum_{j \neq i}^N \sum_{k \neq i}^N \sum_{n_1=1}^{\infty} \cdots \sum_{n_4=1}^{\infty} \frac{S(1, n_1, n_2)(-1)^{n_3+n_4}}{(2n_1-1)!! \cdots (2n_4-1)!!} \\ & \times {}^{(1)}\mathbf{C}_{eeei}^{(1+n_1+n_2)}(\omega) [n_1+n_2] {}^{(n_1)}\mathbf{T}_{ij}^{(n_3)} [n_3] \mathbf{M}_e^{(n_3)}(\mathbf{r}_j) {}^{(n_2)}\mathbf{T}_{ik}^{(n_4)} \times \end{aligned}$$

the induced purely electric and magnetic multipole moments $\mathbf{M}_e^{(n)}(\mathbf{r}, t)$ and $\mathbf{M}_m^{(n)}(\mathbf{r}, t)$ one obtains, respectively, the additional mixed multipole moments $\mathbf{M}_{em}^{(n)}(\mathbf{r}, t)$ and $\mathbf{M}_{me}^{(n)}(\mathbf{r}, t)$. In second-order approximation, $\mathbf{M}_{em}^{(n)}(\mathbf{r}, t)^{(2)}$ consists of a part dependent only on the square of the magnetic field strength and a cross part dependent on the electric and magnetic fields simultaneously. The latter contribution is of the form

$$\begin{aligned} \mathbf{M}_{em}^{(n)}(\mathbf{r}_i, t)^{(2)} = & \frac{1}{2} \sum_{n_1=1}^{\infty} \frac{1}{(2n_1-1)!!} \{ {}^{(n)}_e \mathbf{B}_{emi}^{(1+n_1)}(\omega) + \\ & + {}^{(n)}_e \mathbf{B}_{mei}^{(n_1+1)}(\omega) \} [1+n_1] \mathbf{E}_0(\mathbf{r}_i, t) \mathbf{F}_m^{(n_1)}(\mathbf{r}_i) + \\ & + \frac{1}{2} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{1}{(2n_1-1)!! (2n_2-1)!!} \{ {}^{(n)}_e \mathbf{B}_{emi}^{(n_1+n_2)}(\omega) [n_1+n_2] \times \\ & \times \mathbf{F}_e^{(n_1)}(\mathbf{r}_i, t) \mathbf{F}_m^{(n_2)}(\mathbf{r}_i) + {}^{(n)}_e \mathbf{B}_{mei}^{(n_1+n_2)}(\omega) [n_1+n_2] \times \\ & \times \mathbf{F}_m^{(n_1)}(\mathbf{r}_i) \mathbf{F}_e^{(n_2)}(\mathbf{r}_i, t) \} , \end{aligned} \quad (43)$$

where the $(n+n_1+n_2)$ -rank tensor ${}^{(n)}_e \mathbf{B}_{emi}^{(n_1+n_2)}$ defines the second-order nonlinear 2^n -pole electric polarizability due to 2^{n_1} -pole electric and 2^{n_2} -pole magnetic transitions.

By (18) and (43) we obtain one of the more important cross electro-magnetic contributions to the first-order variation in electric polarizability:

$$\begin{aligned} \Pi_{ei}(\omega)_{NL}^{(1)} = & \frac{1}{2} \sum_{j \neq i} \sum_{n_1=1}^N \sum_{n_2=1}^N \frac{(-1)^{n_2}}{(2n_1-1)!! (2n_2-1)!!} \{ {}^{(1)}_e \mathbf{B}_{emi}^{(1+n_1)} + \\ & + {}^{(1)}_e \mathbf{B}_{mei}^{(n_1+1)}(\omega) \} [n_1] {}^{(n_1)}_i \mathbf{T}_{ij}^{(n_2)} [n_2] \mathbf{M}_m^{(n)}(\mathbf{r}_j). \end{aligned} \quad (44)$$

Analogously, one obtains multipolar mixed electro-magnetic contributions in the third approximations of perturbation theory (see Kielich 1965b).

5. Fundamentals of the statistical-molecular theory of light scattering

5.1 The electric and magnetic multipole fields of the scattered wave

The Liénard-Wiechert potentials generated by a point particle s of the microsystem i at the space-time point $(\mathbf{R}_{si}, t)$ are (De Groot 1969)

$$\begin{aligned} \Phi(\mathbf{R}_{si}, t) &= \frac{e_{si}}{R_{si} + (\mathbf{R}_{si} \cdot \dot{\mathbf{R}}_{si})/c} \Big|_{\text{Ret}}, \\ \mathbf{A}(\mathbf{R}_{si}, t) &= \frac{1}{c} \frac{e_{si} \dot{\mathbf{R}}_{si}}{R_{si} + (\mathbf{R}_{si} \cdot \dot{\mathbf{R}}_{si})/c} \Big|_{\text{Ret}}, \end{aligned} \quad (45)$$

where the subscript 'Ret' indicates that the position $\mathbf{R}_{si}$ and velocity $\dot{\mathbf{R}}_{si}$ must be taken at the retarded moment of time (see figure 1)

$$t' = t - R_{si}(t')/c = t - |\mathbf{r}_i(t') - \mathbf{r}_{si}(t')|/c. \quad (45a)$$

On expanding the potentials (45) in a series in powers of r , and taking into

$$\mathbf{H}^S(\mathbf{r}_i, t) = -\frac{1}{c^2 r_i^2} \{ \mathbf{r}_i \times \ddot{\mathbf{Z}}(t_i) \}_{\text{Ret}}, \quad (46)$$

where

$$t_i = t - r_i/c. \quad (46a)$$

The Hertz vector

$$\mathbf{Z}(t_i) = \mathbf{Z}_e(t_i) + \mathbf{Z}_m(t_i) \quad (47)$$

consists in general of a part accounting for electric multipole radiation (Kielich 1965c)

$$\mathbf{Z}_e(t_i) = \sum_{n=1}^{\infty} \frac{1}{(2n-1)!! r_i^n c^{n-1}} \mathbf{r}_i^{n-1} [n-1] \frac{\partial^{n-1}}{\partial t^{n-1}} \mathbf{M}_e^{(n)}(t_i), \quad (47a)$$

and a part accounting for magnetic multipole radiation

$$\mathbf{Z}_m(t_i) = - \sum_{n=1}^{\infty} \frac{1}{(2n-1)!! r_i^{n+1} c^{n-1}} \mathbf{r}_i^{n-1} [n-1] \left\{ \mathbf{r}_i \times \frac{\partial^{n-1}}{\partial t^{n-1}} \mathbf{M}_m^{(n)}(t_i) \right\}. \quad (47b)$$

5.2 Relation between electric fields in a medium and in vacuum

In the semi-macroscopic approach, we consider a macroscopic sample of volume V , electric permittivity tensor ϵ and magnetic permittivity tensor μ immersed in an isotropic continuous medium with the scalar permittivities ϵ'_0 and μ_0 . The electric field of the light wave in the surrounding medium being $\mathbf{E}_0(\mathbf{r}, t)$, the mean macroscopic (Maxwellian) field $\mathbf{E}(\mathbf{r}, t)$ existing in the sample will in general differ from $\mathbf{E}_0(\mathbf{r}, t)$. The relation between the two fields is dependent on the structure and shape of the sample and the conditions in which the scattered light is observed. Generally, the two fields are related by the tensor $\mathbf{R}_e(\omega)$ as follows (Kielich 1972):

$$\mathbf{E}_0(\mathbf{r}, t) = \mathbf{R}_e(\omega) \cdot \mathbf{E}(\mathbf{r}, t), \quad (48)$$

where

$$\mathbf{R}_e(\omega) = \epsilon_0^{-1} \{ \epsilon_0 \mathbf{U} + \mathbf{L} \cdot [\epsilon(\omega) - \epsilon_0 \mathbf{U}] \}. \quad (48a)$$

Here, $\mathbf{L}$ is a symmetric field depolarization tensor, dependent on the shape of the sample, and defined so that its trace shall equal unity: $\mathbf{L} : \mathbf{U} = L_{xx} + L_{yy} + L_{zz} = 1$. Its principal values are ($\sigma = x, y, z$):

$$L_\sigma = \frac{1}{2} \int_0^\infty \frac{r_x r_y r_z ds}{(r_\sigma^2 + S) [(r_x^2 + S)(r_y^2 + S)(r_z^2 + S)]^{1/2}},$$

r_x, r_y and r_z denoting the principal semi-axes of the ellipsoid. In particular, for a spherical sample $r_x = r_y = r_z = r$ and $\mathbf{L} = \frac{1}{3} \mathbf{U}$, whence the tensor (48a) reduces to

$$\mathbf{R}_e(\omega) = [\epsilon(\omega) + 2\epsilon_0 \mathbf{U}] / 3\epsilon_0. \quad (48b)$$

If moreover the permittivity of the sample is isotropic $\epsilon = \epsilon \mathbf{U}$, one has the well known relation:

$$\mathbf{R}_e(\omega) = [\epsilon(\omega) + 2\epsilon_0] \mathbf{U} / 3\epsilon_0 = \mathbf{R}_e(\omega) \mathbf{U}. \quad (48c)$$

and $L_y = L_z = 1/2$. For a circular oblate disc $L_x = L_y = 0$ and $L_z = 1$.

By analogy to (48) we define the relation tensor $\mathbf{R}_m(\omega)$ between the magnetic vectors $\mathbf{H}_0(\mathbf{r}, t)$ and $\mathbf{H}(\mathbf{r}, t)$.

We now assume that the scattering sample of volume V contains N microsystems, correlated stochastically in time and space. The electric field of light scattered by the spherical sample and observed at a large distance $\mathbf{r}$ in the surrounding medium is (in a satisfactory approximation)

$$\mathbf{E}_0^S(\mathbf{r}, t) = \mathbf{R}_e(\omega_s) \sum_{i=1}^N \mathbf{E}^S(\mathbf{r}_i, t) = \left[\frac{\varepsilon(\omega_s) + 2\varepsilon_0}{3\varepsilon_0} \right] \sum_{i=1}^N \mathbf{E}^S(\mathbf{r}_i, t), \quad (49)$$

where $\varepsilon(\omega_s)$ is the electric permittivity of the isotropic sample at the vibration frequency ω_s of the scattered light wave.

5.3 Intensity of scattered light

We shall now consider the integral intensity of the light scattered by the volume V in order to determine the component thereof transmitted by an analyzer at the point of observation (figure 2). Let the direction of the vibration transmitted by the analyzer be that determined by the unit vector $\mathbf{e}_s$ perpendicular to the vector of observation $\mathbf{r}$. Since now $\mathbf{e}_s \cdot \mathbf{r} = 0$, the component of the electric field (49) in the direction of the unit vector $\mathbf{e}_s$ is, by (46),

$$\mathbf{E}_0^S(\mathbf{r}, t) \cdot \mathbf{e}_s = -\frac{1}{c^2} R_e(\omega_s) \sum_{i=1}^N \ddot{\mathbf{Z}}(t_i) \cdot \mathbf{e}_s. \quad (49a)$$

The intensity of the light scattered by the volume V and transmitted by an analyzer outside the sample at r is defined as follows:

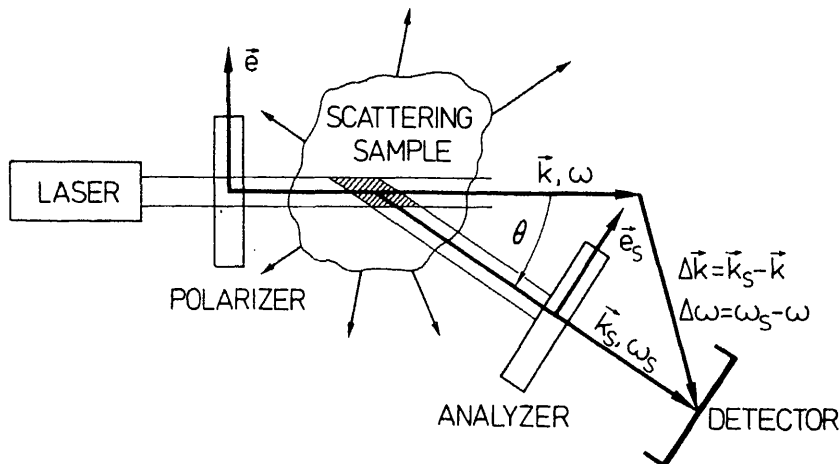


Figure 2. Laser light scattering experiment. The incident laser light beam has the frequency ω , propagation vector $\mathbf{k}$ and polarization vector $\mathbf{e}$, whereas the scattered beam has the frequency ω_s , propagation vector $\mathbf{k}_s$ and polarization vector $\mathbf{e}_s$; $\Delta\mathbf{k} = \mathbf{k}_s - \mathbf{k}$ is the scattering vector and θ the scattering angle.

where the symbol $\langle \rangle$ denotes appropriate statistical averaging.

Substituting (49a) in (50), the fundamental equation for the scattered intensity takes the form

$$I_{e,e}(r) = \frac{R_e^2(\omega_s)}{8\pi c^3} \left\langle \sum_{i=1}^N \sum_{j=1}^N \mathbf{e}_s \cdot \ddot{\mathbf{Z}}(t_i)^* \ddot{\mathbf{Z}}(t_j) \cdot \mathbf{e}_s^* \right\rangle, \quad (50a)$$

where the Hertz vector is given by (47).

Since by assumption $V \ll \lambda^3$, we can restrict our considerations to light scattering of the electric dipolar type. We now have by (34), (47) and (50a):

$$I_{e,e}(r) = Q(\omega_s) I_0 \left\langle \sum_{i=1}^N \sum_{j=1}^N [\mathbf{e}_s \cdot \Pi_{ei}(\omega)^* \cdot \mathbf{e}^*] \times \right. \\ \left. \times [\mathbf{e} \cdot \Pi_{ej}(\omega) \cdot \mathbf{e}_s^*] \exp(i\Delta \mathbf{k} \cdot \mathbf{r}_{ij}) \right\rangle, \quad (50b)$$

where I_0 is the incident light intensity existing within the scattering sample and $Q(\omega_s) = (1/r^2)(\omega_s/c)^4 R_e^2(\omega_s) R_e^2(\omega)$.

In the case of an isotropic medium and when the external field is absent, the probability for all directions of the unit vectors $\mathbf{e}$ and $\mathbf{e}_s$ is the same, so it is useful first to perform unweighted averaging in (50b) over all possible orientations of $\mathbf{e}$ and $\mathbf{e}_s$ with respect to the fixed system of reference (X, Y, Z) :

$$I_{e,e}(r) = I_{e,e}^{\text{is}} + I_{e,e}^{\text{antis}} + I_{e,e}^{\text{anis}}, \quad (51)$$

where we have the intensities of isotropic, antisymmetric and anisotropic scattering, respectively, in the form

$$I_{e,e}^{\text{is}} = \frac{1}{3} Q(\omega_s) I_0 S^{\text{is}} |\mathbf{e}_s \cdot \mathbf{e}^*|^2, \quad (51a)$$

$$I_{e,e}^{\text{antis}} = \frac{1}{6} Q(\omega_s) I_0 S^{\text{antis}} (1 - |\mathbf{e}_s \cdot \mathbf{e}^*|^2), \quad (51b)$$

$$I_{e,e}^{\text{anis}} = \frac{1}{30} Q(\omega_s) I_0 S^{\text{anis}} (3 + 3|\mathbf{e}_s \cdot \mathbf{e}^*|^2 - 2|\mathbf{e}_s \cdot \mathbf{e}^*|^2). \quad (51c)$$

Above, we have introduced the constants

$$S^{\text{is}} = \left\langle \sum_{i=1}^N \sum_{j=1}^N \Pi_{ei}(\omega)^* \Pi_{ej}(\omega) \exp(i\Delta \mathbf{k} \cdot \mathbf{r}_{ij}) \right\rangle, \quad (52)$$

$$S^{\text{antis}} = \left\langle \sum_{i=1}^N \sum_{j=1}^N \Pi_{ei}^{\text{antis}}(\omega) : \Pi_{ej}^{\text{antis}}(\omega) \exp(i\Delta \mathbf{k} \cdot \mathbf{r}_{ij}) \right\rangle, \quad (53)$$

$$S^{\text{anis}} = \left\langle \sum_{i=1}^N \sum_{j=1}^N \{ \Pi_{ei}(\omega)^* : \Pi_{ej}(\omega) - 3\Pi_{ei}(\omega)^* \Pi_{ej}(\omega) \} \exp(i\Delta \mathbf{k} \cdot \mathbf{r}_{ij}) \right\rangle, \quad (54)$$

characterizing the molecular-statistical mechanism of isotropic, antisymmetric and anisotropic scattering.

Here, we have introduced a scalar polarizability:

$$\Pi_{ei} = \frac{1}{3} \Pi_{ei} : \mathbf{U}. \quad (52a)$$

definition ($h = 0, 1, 2$):

$$S^{(h)} = \left\langle \sum_{i=1}^N \sum_{j=1}^N \Pi_{ei}^{(h)}(\omega) : \Pi_{ej}^{(h)}(\omega) \exp(i\Delta \mathbf{k} \cdot \mathbf{r}_{ij}) \right\rangle \quad (55)$$

in agreement with the fact that a second-rank tensor can be represented in the form of the sum of three irreducible components:

$$\Pi = \Pi^{(0)} + \Pi^{(1)} + \Pi^{(2)} = \sum_{h=0}^2 \Pi^{(h)},$$

where $\Pi^{(0)} = \Pi U$ is an isotropic tensor ($h=0$), $\Pi^{(1)}$ an antisymmetric tensor ($h=1$) and $\Pi^{(2)}$ an anisotropic tensor ($h=2$). So, in this way, we can denote $S^{\text{is}} = S^{(0)}$, $S^{\text{antis}} = S^{(1)}$ and $S^{\text{anis}} = S^{(2)}$ (see Placzek 1934).

With regard to the perturbation expansion of the polarizability tensor (35), we rewrite the scattering constants (55) as follows:

$$S^{(h)} = \sum_{p=0}^{\infty} S_p^{(h)} = S_0^{(h)} + S_1^{(h)} + S_2^{(h)} + \dots, \quad (55a)$$

where

$$S_p^{(h)} = \sum_{q=0}^p \left\langle \sum_{i=1}^N \sum_{j=1}^N \Pi_{ei}^{(h)}(\omega)^{(q)} : \Pi_{ej}^{(h)}(\omega)^{(p-q)} \exp(i\Delta \mathbf{k} \cdot \mathbf{r}_{ij}) \right\rangle \quad (55b)$$

is the h -scattering constant of the n th approximation. In general, the above statistical averaging should be performed with the grand canonical statistical ensemble

$$f(\mathbf{r}^N, \Omega^N) = Q_N \exp \{ -(U^N + H^N)/kT \}, \quad (56)$$

where, in addition to the long-range interaction Hamiltonian of multipole interactions of N microsystems, we have the potential energy U^N of short-range interactions of the N multipolar microsystems.

The various kinds of molecular energies have recently been reviewed by Ratajczak and Orville-Thomas (1980).

6. Angular distribution and polarization states of scattered light

Let us assume a set-up in which the incident light propagates along the Z -axis of laboratory coordinates XYZ , attached to the centre of the scattering volume V (figure 3). The scattered light is observed in a distinct set of laboratory co-ordinates $X'Y'Z'$. As the plane of observation we chose the $Y'Z'$ -plane, which coincides with the YZ -plane. Thus, Θ is our scattering angle, subtended by the axes Z and Z' .

Generally, we express the versor $\mathbf{e}$ of the incident wave electric field $\mathbf{E} = E\mathbf{e}$ as follows:

$$\mathbf{e} = \mathbf{x} \sin \Psi + e^{i\Delta} \mathbf{y} \cos \Psi, \quad (57)$$

where Ψ is the angle between $\mathbf{e}$ and the YZ -plane, and Δ is the phase shift of the Y -component of the field $\mathbf{E}$ ($\mathbf{x}, \mathbf{y}, \mathbf{z}$ are unit vectors in the direction of the axes X, Y, Z of the laboratory frame).

The unit vector $\mathbf{e}_s$ defining the polarization of the scattered beam in co-ordinates $X'Y'Z'$ can in general be written in a form similar to (57):

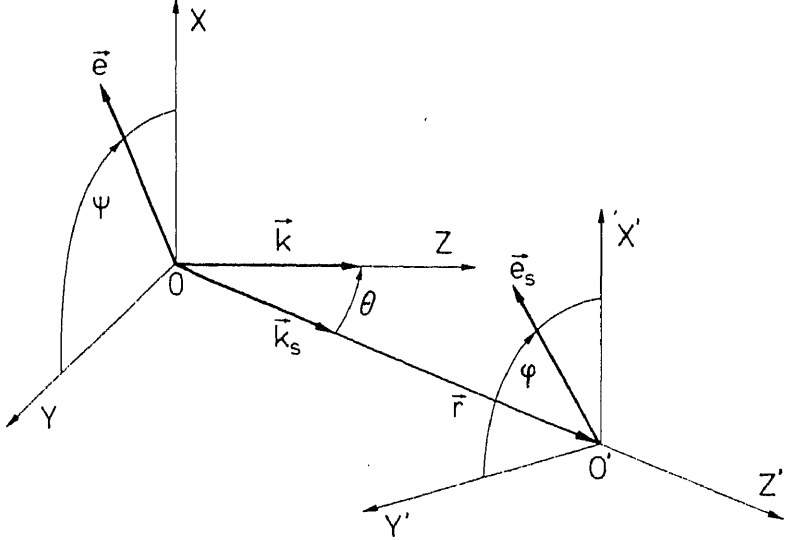


Figure 3. Systems for the determination of the angular distribution and polarization states of scattered beams.

$$\mathbf{e}_s = x \sin \varphi + e^{i\delta} (y \cos \Theta - z \sin \Theta) \cos \varphi, \quad (58)$$

φ being the angle between $\mathbf{e}_s$ and the $Y'Z'$ plane.

Equations (57) and (58) account for all possible states of polarization of the incident and scattered light. For example, at $\Delta = 0$ the incident wave is linearly polarized at an arbitrary angle

$$\mathbf{e} = x \sin \Psi + y \cos \Psi. \quad (57a)$$

If the y -component of the field is shifted in phase by $\Delta = \pm \pi/2$, we have for elliptical polarization

$$\mathbf{e}_{\pm} = x \sin \Psi \pm iy \cos \Psi, \quad (57b)$$

where with regard to the angular momentum convention a phase shift $+\pi/2$ refers to right circular polarization of the wave and $-\pi/2$ to left circular polarization. If in addition $\Psi = \pi/4$, then (57b) gives for a circularly polarized wave

$$\mathbf{e}_{\pm} = (x \pm iy)/\sqrt{2}. \quad (57c)$$

It is our aim to determine the angular distribution and polarization state of the intensity scattering components (51a)–(51c).

6.1 Linearly polarized incident light

For linearly polarized incident light, we have by (57a) and (58)

$$|\mathbf{e}_s \cdot \mathbf{e}^*|^2 = |\mathbf{e}_s \cdot \mathbf{e}|^2 = \sin^2 \varphi \cos^2 \Psi + \cos^2 \Theta \cos^2 \varphi \cos^2 \Psi +$$

and obtain from (51a)–(51c) for the vertical and horizontal scattered intensity components (see figure 4)

$$I_{VV}^{is} = \frac{1}{3} Q(\omega_s) S^{(0)}, \quad I_{HV}^{is} = I_{VH}^{is} = 0, \\ I_{HH}^{is} = \frac{1}{3} Q(\omega_s) S^{(0)} \cos^2 \Theta, \quad (59a)$$

$$I_{VV}^{antis} = 0, \quad I_{HV}^{antis} = I_{VH}^{antis} = \frac{1}{6} Q(\omega_s) S^{(1)}, \\ I_{HH}^{antis} = \frac{1}{6} Q(\omega_s) S^{(1)} (1 - \cos^2 \Theta), \quad (59b)$$

$$I_{VV}^{anis} = \frac{2}{15} Q(\omega_s) S^{(2)}, \\ I_{HV}^{anis} = I_{VH}^{anis} = \frac{1}{10} Q(\omega_s) S^{(2)}, \\ I_{HH}^{anis} = \frac{1}{30} Q(\omega_s) S^{(2)} (3 + \cos^2 \Theta). \quad (59c)$$

Defining the depolarization rates as $D_V = I_{HV}^s / I_{VV}^s$ and $D_H = I_{VH}^s / I_{HH}^s$ for incident light polarized vertically ($\Psi = 90^\circ$) or horizontally ($\Psi = 0^\circ$), respectively, we obtain by (59a)–(59c):

$$D_V = \frac{3S^{(2)} + 5S^{(1)}}{10S^{(0)} + 4S^{(2)}}, \quad (60a)$$

$$D_H(\Theta) = \frac{3S^{(2)} + 5S^{(1)}}{10S^{(0)} \cos^2 \Theta + 5S^{(1)} (1 - \cos^2 \Theta) + S^{(2)} (3 + \cos^2 \Theta)}. \quad (60b)$$

Equation (60a) is similar to the result derived by Placzek (1934) for Raman scattering.

6.2 Circularly polarized incident light

In the case of circularly polarized incident light (57c) we obtain by (58) from (51a)–(51c):

$$I_{e,\pm 1}^{is} = \frac{1}{6} Q(\omega_s) S^{(0)} (\sin^2 \varphi + \cos^2 \Theta \cos^2 \varphi \pm \cos \Theta \sin 2\varphi \sin \delta), \quad (61a)$$

$$I_{e,\pm 1}^{antis} = \frac{1}{12} Q(\omega_s) S^{(1)} (2 - \sin^2 \varphi - \cos^2 \Theta \cos^2 \varphi \pm \cos \Theta \sin 2\varphi \sin \delta), \quad (61b)$$

$$I_{e,\pm 1}^{anis} = \frac{1}{60} Q(\omega_s) S^{(2)} (6 + \sin^2 \varphi + \cos^2 \Theta \cos^2 \varphi \mp 5 \cos \Theta \sin 2\varphi \sin \delta). \quad (61c)$$

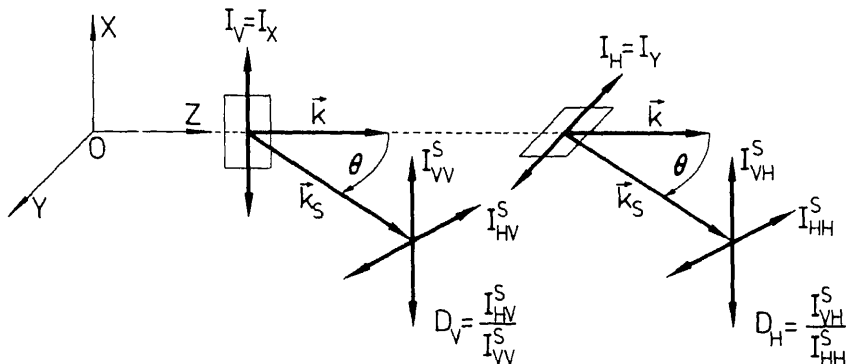


Figure 4. The incident light beam propagates along the Z-axis with intensities I_V or I_H ,

The depolarization ratio is usually defined as the ratio of the lowest $I_{H\pm 1}$ and highest $I_{V\pm 1}^S$ possible values of the scattered intensity (see Born 1933). We obtain by (61) at $\delta = 0$ and $\varphi = 0^\circ$ or $\varphi = 90^\circ$:

$$D_{\pm 1}(\Theta) = \frac{10S^{(1)} + 6S^{(2)} + (10S^{(0)} - 5S^{(1)} + S^{(2)})\cos^2 \Theta}{10S^{(0)} + 5S^{(1)} + 7S^{(2)}}. \quad (62)$$

For incident light circularly polarized in the right sense only ($e = +1$), we obtain by eqs (61) for $\delta = \pm \pi/2$, $\varphi = \pi/4$ and $e_s = \pm 1$:

$$I_{\pm 1 \pm 1}^{\text{is}} = \frac{1}{12} Q(\omega_s) S^{(0)} (1 \pm \cos \Theta)^2, \quad (63a)$$

$$I_{\pm 1 \pm 1}^{\text{antis}} = \frac{1}{24} Q(\omega_s) S^{(1)} [4 - (1 \mp \cos \Theta)^2], \quad (63b)$$

$$I_{\pm 1 \pm 1}^{\text{anis}} = \frac{1}{120} Q(\omega_s) S^{(2)} (13 \mp 10 \cos \Theta + \cos^2 \Theta). \quad (63c)$$

The reversal ratio is by definition the ratio of that part of the scattered intensity whose sense of circular polarization is contrary to that of the incident wave and the part whose sense of circular polarization coincides with the latter (see figure 5). We thus have, quite generally,

$$R_{\pm 1} = \frac{I_{\mp 1 \pm 1}^S}{I_{\pm 1 \pm 1}^S},$$

and obtain by (63) for right-circularly polarized incident light:

$$R_{+1}(\Theta) = \frac{40S^{(0)} \sin^4 \Theta/2 + 20S^{(1)}(1 - \cos^4 \Theta/2) + S^{(2)}(13 + 10 \cos \Theta + \cos^2 \Theta)}{40S^{(0)} \cos^4 \Theta/2 + 20S^{(1)}(1 - \sin^4 \Theta/2) + S^{(2)}(13 - 10 \cos \Theta + \cos^2 \Theta)}. \quad (64)$$

In the case of forward scattering ($\Theta = 0^\circ$), eq. (64) reduces to (see Placzek 1934)

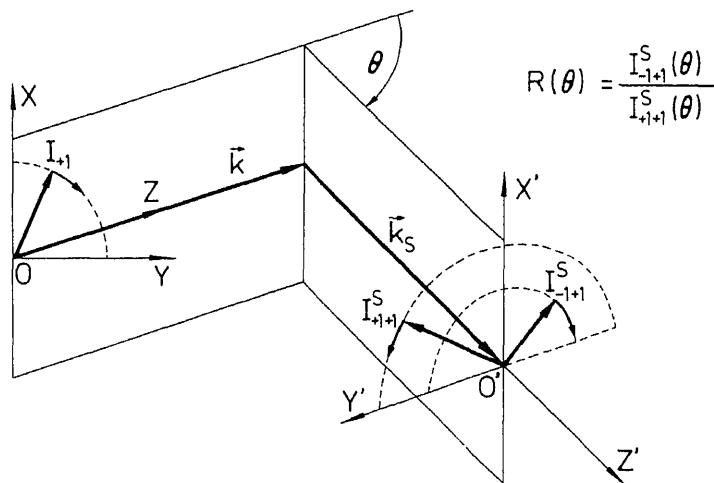


Figure 5. Geometry for the determination of the reversal ratio, on the angular momentum convention. Under the action of the right circularly polarized incident beam I_{+1} propagating along the Z -axis, two circularly polarized components appear in the scattered beam, the one

$$R_{+1}(0^\circ) = \frac{6S^{(2)}}{10S^{(0)} + 5S^{(1)} + S^{(2)}}, \quad (64a)$$

which in some special cases yields results well known from the literature (Born 1933; Long 1977).

7. Application to isotropic scattering

The subsequent discussion of our theory consists in applications of the scattering constants (52)–(54) to particular situations, disclosing the optical properties of the microsystems as such, as well as the micro-structure and thermodynamical state of various substances. We first proceed to consider the isotropic scattering constant (52).

7.1 Microsystems exhibiting constant polarizability

If the scattering medium is but a moderately condensed one, the effect of the long range intermolecular field on the polarizability tensor of the microsystem may be neglected in the expansion (35), and the expression (52) may be written in the zeroth approximation as follows:

$$S_0^{\text{is}} = 3 \left\langle \sum_{i=1}^N \sum_{j=1}^N A_{ei}^* A_{ej} \exp(i \Delta \mathbf{k} \cdot \mathbf{r}_{ij}) \right\rangle, \quad (65)$$

where A_{ei} denotes the mean electric polarizability of the isolated i th microsystem.

We decompose the scattering constant (65) into an incoherent part ($i = j$)

$$S_{0,\text{inc}}^{\text{is}} = 3 \sum_{i=1}^N |A_{ei}|^2 \quad (65a)$$

describing scattering by statistically independent microsystems, and a coherent part ($i \neq j$)

$$S_{0,\text{coh}}^{\text{is}} = 3 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* A_{ej} \frac{\sin \Delta k r_{ij}}{\Delta k r_{ij}} \right\rangle \quad (65b)$$

describing scattering by stochastically correlated microsystems.

If all the microsystems present within the scattering volume V are of one kind $A_{ei} = A_{ej} = A_e$, then (65a) and (65b) may be rewritten as follows:

$$S_{0,\text{inc}}^{\text{is}} = 3N |A_e|^2, \quad (65c)$$

$$S_{0,\text{coh}}^{\text{is}} = S_{0,\text{inc}}^{\text{is}} \Gamma(\Delta \mathbf{k}), \quad (65d)$$

where we have the integral parameter

$$\Gamma(\Delta \rho) = k \int_0^\infty \iint \left\{ g^{(2)}(r_{12}, \Omega_1, \Omega_2) - 1 \right\} \frac{\sin \Delta k r_{12}}{\Delta k r_{12}} d\mathbf{r}_{12} d\Omega_1 d\Omega_2, \quad (66)$$

introduced by Zernike and Prins (1927) in their theory of x-ray scattering by liquids. Above, $g^{(2)}(r_{12}, \Omega_1, \Omega_2)$ is the binary correlation function for microsystems 1 and 2 having orientations Ω_1 and Ω_2 at the distance r_{12} , and $\rho = N/V$ is the number density

$$\Gamma(0) = N^{-1} \langle (\Delta N)^2 \rangle - 1, \quad (66b)$$

where the mean square fluctuation of the number of microsystems is given by the Smoluchowski-Einstein formula

$$\langle (\Delta N)^2 \rangle = V \rho^2 kT \beta_T$$

with β_T —the isothermal compressibility coefficient of the medium.

In the case of compressed gases, we have by (66) the relation

$$\Gamma(0) = -\frac{1}{2} B(T) \quad (66c)$$

between $\Gamma(0)$ and the second virial coefficient of the equation of state of the real gas

$$B(T) = -\frac{2\pi N}{\Omega^2} \int_0^\infty \iint \{ \exp[-u(r_{12}, \Omega_1, \Omega_2)/kT] - 1 \} r_{12}^2 dr_{12} d\Omega_1, d\Omega_2, \quad (67)$$

where $u(r_{12}, \Omega_1, \Omega_2)$ denotes the total potential energy of interaction of the two microsystems.

Hence, it is obvious that coherent isotropic scattering is accounted for directly by the second virial coefficient (67) only if the microsystems exhibit a polarizability that is unaffected by the presence of their neighbours. Perturbation series expansions of the second virial coefficient (67) for general multipole interactions have, of course, been considered by many authors (see *eg* Kielich 1965f; Stogryn 1969; Moraal 1976; Singh and Singh 1976; Isnard *et al* 1980).

7.2 Microsystems with variable polarizability

In a sufficiently condensed medium, the polarizability of a microsystem is affected by the presence of the intrinsic fields of its neighbours.

Let us first calculate the contribution to (52) for the case when the statistical averaging is performed with the distribution function (56) in the absence of tensorial interaction

$$f(\mathbf{r}^N, \Omega^N) = \Omega^{-N} f(\mathbf{r}^N), \quad (56a)$$

so we have only radial molecular interactions described by the potential energy $U_0(\mathbf{r}^N)$.

Under the assumption of (56a), the first approximation of (55b) vanishes. In the second approximation we have by (52) and (55b):

$$S_{0, \text{coh}}^{\text{is}} = S_{02}^{\text{is}} + S_{11}^{\text{is}} + S_{20}^{\text{is}}, \quad (68)$$

where we have, in the absence of interference effects,

$$S_{02}^{\text{is}} = 3 \left\langle \sum_{i=1}^N \sum_{j=1}^N \Pi_{ei}^{(0)*} \Pi_{ej}^{(2)} \right\rangle, \quad (68a)$$

$$S_{11}^{\text{is}} = 3 \left\langle \sum_{i=1}^N \sum_{j=1}^N \Pi_{ei}^{(1)*} \Pi_{ej}^{(1)} \right\rangle, \quad (68b)$$

and S_{20}^{is} is defined similarly to S_{02}^{is} .

$$\begin{aligned}
{}_2S_{02}^{\text{is}} = & \sum_{n=1}^{\infty} \sum_{u=1}^{\infty} \frac{2^{n+u}(n! u!)^2 (2n+2u)!}{(2n)!(2n+1)![(2u)!]^2} \times \\
& \times \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* \{ A_{ei}^{(2u)} ({}^{(1)}\mathbf{A}_{ej}^{(n)} [n+1] {}^{(n)}\mathbf{A}_{ej}^{(1)}) + \right. \\
& \left. + A_{ej}^{(2u)} ({}^{(1)}\mathbf{A}_{ei}^{(n)} [n+1] {}^{(n)}\mathbf{A}_{ei}^{(1)}) \} r_{ij}^{-2(n+u+1)} \right\rangle, \quad (69)
\end{aligned}$$

and, for the three-body correlations contribution:

$$\begin{aligned}
{}_3S_{02}^{\text{is}} = & \sum_{n=1}^{\infty} (n+1)!(2n+1) \frac{2^n n!}{(2n)!} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N \times \right. \\
& \times (A_{ei}^* + A_{ej}^* + A_{ek}^*) A_{ei} A_{ej}^{(2n)} A_{ek} (r_{ij} r_{jk})^{-(n+2)} P_{n+1} \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) \Bigg\rangle \\
& + \sum_{n=1}^{\infty} \sum_{u=1}^{\infty} \frac{2^{n+u}(n! u!)^2 (2n+2u)!}{(2n)!(2n+1)![(2u)!]^2} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N \times \right. \\
& \times A_{ei}^* \{ {}^{(1)}\mathbf{A}_{ej}^{(n)} [n+1] {}^{(n)}\mathbf{A}_{ej}^{(1)} \} A_{ek}^{(2u)} r_{jk}^{-2(n+u+1)} \Bigg\rangle. \quad (70)
\end{aligned}$$

Here,

$$A_{ei}^{(2n)} = \frac{1}{2n+1} {}^{(n)}\mathbf{A}_{ei}^{(n)} [2n] \mathbf{U}^n \quad (71)$$

is the mean value of the 2^n -pole electric polarizability of the i th microsystem and P_{n+1} is a Legendre polynomial of degree $n+1$.

The contribution (69) is similar to that obtained previously by Kielich (1965a, b) for molecular refraction and distortional electric polarization but the contribution (70) differs by the last term, proportional to $r_{jk}^{-2(n+u+1)}$.

If the higher-order terms are neglected, we obtain from (69)

$$\begin{aligned}
{}_2S_{02}^{\text{is}} = & 2 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* \{ [A_{ei}(\mathbf{A}_{ej} : \mathbf{A}_{ej}) + (\mathbf{A}_{ei} : \mathbf{A}_{ei}) A_{ej}] r_{ij}^{-6} + \right. \\
& + [A_{ei} ({}^{(1)}\mathbf{A}_{ej}^{(2)} : {}^{(2)}\mathbf{A}_{ej}^{(1)}) + ({}^{(1)}\mathbf{A}_{ei}^{(2)} : {}^{(2)}\mathbf{A}_{ei}^{(1)}) A_{ej}] r_{ij}^{-8} + \\
& + \frac{4}{5} [A_{ei} ({}^{(1)}\mathbf{A}_{ej}^{(3)} : {}^{(3)}\mathbf{A}_{ej}^{(1)}) + ({}^{(1)}\mathbf{A}_{ei}^{(3)} : {}^{(3)}\mathbf{A}_{ei}^{(1)}) A_{ej}] r_{ij}^{-10} + \\
& + \frac{5}{3} [A_{ei}^{(4)} (\mathbf{A}_{ej} : \mathbf{A}_{ej}) + (\mathbf{A}_{ei} : \mathbf{A}_{ei}) A_{ej}^{(4)}] r_{ij}^{-8} + \\
& \left. + \frac{28}{9} [A_{ei}^{(4)} ({}^{(1)}\mathbf{A}_{ej}^{(2)} : {}^{(2)}\mathbf{A}_{ej}^{(1)}) + ({}^{(1)}\mathbf{A}_{ei}^{(2)} : {}^{(2)}\mathbf{A}_{ei}^{(1)}) A_{ej}^{(4)}] r_{ij}^{-10} + \dots \} \right\rangle, \quad (69a)
\end{aligned}$$

where ${}^{(1)}\mathbf{A}_{ei}^{(2)}$ and ${}^{(2)}\mathbf{A}_{ei}^{(1)}$ are the linear electric dipole-quadrupole and quadrupole-dipole polarizabilities and, by (71), $A_{ei}^{(4)}$ is the mean electric quadrupole-quadrupole polarizability.

As a particular case of some interest we shall consider that of axially-symmetric molecules with centers of inversion for which (69a) yields in a good approximation

$${}_2S_{02}^{\text{is}} = 6 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* \{ A_{ei} A_{ej} [A_{ei}(1+2\kappa_i^2) + A_{ej}(1+2\kappa_j^2)] r_{ij}^{-6} + \right. \\ \left. + \frac{2}{3} [A_{ei}^{(4)} A_{ej}^2 (1+2\kappa_j^2) + A_{ei}^2 (1+2\kappa_i^2) A_{ej}^{(4)}] r_{ij}^{-8} + \dots \} \right\rangle, \quad (69b)$$

where $\kappa \equiv (A_{\parallel} - A_{\perp})/3A$ is a parameter determining the anisotropy of dipole polarizability with $A_{\parallel}$ and $A_{\perp}$, respectively, the polarizability in the directions parallel and perpendicular to the molecule's symmetry axis.

In the same manner we can particularize the three-body contribution (70); *e.g.* we have for the electric dipole approximation

$${}_3S_{02}^{\text{is}} = 2 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N \left\{ 3(A_{ei}^* + A_{ej}^* + A_{ek}^*) A_{ei} A_{ej} A_{ek} \cdot \right. \right. \\ \left. \times (r_{ij} r_{jk})^{-3} P_2 \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) + A_{ei}^* A_{ek} (\mathbf{A}_{ej} : \mathbf{A}_{ej}) r_{jk}^{-6} \right\} \right\rangle. \quad (70a)$$

In the calculation of the contribution (68b) we restrict ourselves to the electric dipole-dipole approximation in the multipole expansion (36) and obtain for the two- and three-body interactions

$${}_2S_{11}^{\text{is}} = \frac{1}{75} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \{ 60[|A_{ei}|^2 (\mathbf{D}_{ej}^* : \mathbf{D}_{ej}) + (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) |A_{ej}|^2] + \right. \\ \left. + 7(\mathbf{D}_{ei}^* : \mathbf{D}_{ei})(\mathbf{D}_{ej}^* : \mathbf{D}_{ej}) \} r_{ij}^{-6} \right\rangle, \quad (72a)$$

$${}_3S_{11}^{\text{is}} = \frac{4}{5} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N \{ A_{ei}^* A_{ek} + A_{ei} A_{ek}^* \} (\mathbf{D}_{ej}^* : \mathbf{D}_{ej}) \times \right. \\ \left. \times (r_{ij} r_{jk})^{-3} P_2 \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) \right\rangle, \quad (72b)$$

with

$$\mathbf{D}_e = \mathbf{A}_e - A_e \mathbf{U} \quad (71a)$$

the deviation tensor of linear dipole-dipole electric polarizability.

Applying the preceding expression to axially-symmetric molecules, we obtain:

$${}_2S_{11}^{\text{is}} = \frac{12}{5} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N |A_{ei}|^2 |A_{ej}|^2 (2\kappa_i^2 + 2\kappa_j^2 + \frac{7}{5}\kappa_i^2 \kappa_j^2) r_{ij}^{-6} \right\rangle, \quad (72c)$$

$${}_3S_{11}^{\text{is}} = \frac{24}{5} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N (A_{ei}^* A_{ek} + A_{ei} A_{ek}^*) |A_{ej}|^2 \kappa_j^2 \times \right. \\ \left. \times (r_{ij} r_{jk})^{-3} P_2 \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) \right\rangle. \quad (72d)$$

$$\begin{aligned}
{}_4S_{02}^{\text{is}} = 6 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N \sum_{l \neq k \neq j \neq i}^N A_{ei}^* A_{ej} A_{ek} A_{el} \times \right. \\
\left. \times r_{jk}^{-3} r_{kl}^{-3} P_2 \left(\frac{\mathbf{r}_{jk} \cdot \mathbf{r}_{kl}}{r_{jk} r_{kl}} \right) \right\rangle. \quad (72f)
\end{aligned}$$

On proceeding to the next higher dipole-quadrupole approximation in the expansion (36) we obtain, beside the two-body contribution provided by (69a):

$$\begin{aligned}
{}_2S_{02}^{\text{is}} = 2 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \{ |A_{ei}|^2 ({}^{(1)}\mathbf{A}_{ej}^{(2)} : {}^{(2)}\mathbf{A}_{ej}^{(1)}) + \right. \\
\left. + ({}^{(1)}\mathbf{A}_{ei}^{(2)} : {}^{(2)}\mathbf{A}_{ei}^{(1)}) A_{ei}^* A_{ej} \} r_{ij}^{-8} \right\rangle, \quad (69c)
\end{aligned}$$

the following contributions arising from (68b) for the two- and three-body interactions (Kielich 1980)*

$${}_2S_{11}^{\text{is}} = \frac{40}{21} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \{ |A_{ei}|^2 G_j^{(3,3)} + \frac{2}{25} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) K_j^{(3,3)} \} r_{ij}^{-8} \right\rangle \quad (72f)$$

$${}_3S_{11}^{\text{is}} = -\frac{40}{21} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N A_{ei}^* G_j^{(3,3)} A_{ek} \cdot r_{ij}^{-4} r_{jk}^{-4} P_3 \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) \right\rangle, \quad (72g)$$

$${}_4S_{11}^{\text{is}} = 0, \quad (72h)$$

where the molecular parameters $G_j^{(3,3)}$ and $K_j^{(3,3)}$ are in general rather highly complicated combinations of scalar products of the tensors ${}^{(1)}\mathbf{A}_j^{(2)}$ and ${}^{(2)}\mathbf{A}_j^{(1)}$ and we refrain from adducing them in explicit form. We shall consider these formulae again in §8.

7.2b. Nonlinear multipole polarizabilities: We now consider the higher contributions to (68) from the nonlinear multipole polarizabilities (40) and (42). By (42) we obtain for the two-body contribution (Kielich 1965b)

$$\begin{aligned}
{}_2S_{02}^{\text{is}} = \frac{1}{2} \sum_{n=1}^{\infty} \sum_{u=1}^{\infty} \frac{2^{n+u} (n! u!)^2 (2n+2u)! (2n+3)}{(2n)! (2n+1)! (2u)! (2u+1)!} \times \\
\times \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* \{ C_{ei}^{2(n+1)} (\mathbf{M}_{ej}^{(u)} [u] \mathbf{M}_{ej}^{(u)}) + \right. \\
\left. + (\mathbf{M}_{ei}^{(u)} [u] \mathbf{M}_{ei}^{(u)}) C_{ej}^{2(n+1)} \} r_{ij}^{-2(n+u+1)} \right\rangle, \quad (73)
\end{aligned}$$

where

$$C_{ei}^{2(n+1)} = \frac{1}{2n+3} \mathbf{U} : {}^{(1)}\mathbf{C}_{eee}^{(1+n+n)} [2n] \mathbf{U}^n \quad (74)$$

is the mean nonlinear (third order) multipole electric polarizability

In the case of axially-symmetric molecules possessing only the third-order mean dipole-dipole polarizability $C_e^{(4)}$, the expression (73) becomes

$${}_2S_{02}^{\text{is}} = \frac{2}{3} \sum_{n=1}^{\infty} (n+1) \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* \{ C_{ei}^{(4)} (M_{ej}^{(n)})^2 + (M_{ei}^{(n)})^2 C_{ej}^{(4)} \} r_{ij}^{-2(n+2)} \right\rangle, \quad (73a)$$

where, by (9),

$$M_{ei}^{(n)} = \sum_{s=1}^{n_1} e_{si} r_{si}^n P_n(\cos \Theta_s) \quad (9a)$$

is the 2^n -pole scalar electric moment of an axially symmetric i th molecule.

By (40b), we obtain for nonlinearly polarizable dipolar and quadrupolar molecules, respectively (Kielich 1980)

$${}_2S_{02}^{\text{is}} = 2 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* (A_{ei} + A_{ej}) (\mathbf{U} : {}^{(1)}_e \mathbf{B}_{eej}^{(1+1)} : \mathbf{M}_{ej}^{(1)}) r_{ij}^{-6} \right\rangle, \quad (75a)$$

$${}_2S_{02}^{\text{is}} = 2 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* (A_{ei} + A_{ej}) (\mathbf{U} : {}^{(1)}_e \mathbf{B}_{eej}^{(1+2)} : \mathbf{M}_{ej}^{(2)}) r_{ij}^{-8} \right\rangle. \quad (75b)$$

The molecular parameter $\mathbf{U} : {}^{(1)}_e \mathbf{B}_{ee}^{(1+1)} : \mathbf{M}_e^{(1)}$ intervenes in DC electric field-induced second-harmonic light generation (Kielich 1969, 1979; Hauchecorne *et al* 1971) permitting the determination of the value of the nonlinear (second-order) dipole-dipole electric polarizability tensor ${}^{(1)}_e \mathbf{B}_{ee}^{(1+1)}$, if the intrinsic electric dipole moment $\mathbf{M}_e^{(1)}$ is known. The new contributions (75a) and (75b) are of interest as containing the first power of the tensors ${}^{(1)}_e \mathbf{B}_{ee}^{(1+1)}$ and ${}^{(1)}_e \mathbf{B}_{ee}^{(1+2)}$ and not their square, as it is the case for the S_{11}^{is} contribution (Kielich 1960, 1968). So the formula (75b) provides an indirect method for the determination of the value and sign of the second-order nonlinear dipole-quadrupole electric polarizability or the intrinsic quadrupole electric moment $\mathbf{M}_e^{(2)}$.

7.3 Temperature-dependent contributions arising from electrostatic multipole interaction

Hitherto, in the foregoing calculations, we considered the approximation (56a) when the distribution function depended only on the positional variables $\mathbf{r}^N$ of the molecules. Generally, the total interaction energy consists, besides $U_0(\mathbf{r}^N)$, also of that part of $V_\Omega^N = V(\mathbf{r}^N, \Omega^N)$ which depends both on the positional and orientational variables $\mathbf{r}$ and Ω of the molecules. In the case of weak tensorial interactions between the microsystems, i.e. when simultaneously $V_\Omega \ll U_0$ and $V_\Omega < kT$, the Boltzmann factors in (56) can be expanded in power series in V_Ω/kT . In particular, restricting the problem to the first approximation of statistical perturbation calculus, the exact distribution function (56) can be replaced by:

$$f(\mathbf{r}^N, \Omega^N) = \Omega^{-N} f(\mathbf{r}^N) \left\{ 1 - \frac{1}{kT} (V_\Omega - \langle V_\Omega \rangle) + \dots \right\}. \quad (56b)$$

mainly, electrostatic multipole interactions in (17) play the predominant role and we obtain for dipole-quadrupole type interactions with regard to (36) and (56b) (Kielich 1960)

$${}_2S_{01(1)}^{\text{is}} = -\frac{1}{5kT} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N (A_{ei}^* + A_{ej}^*) (\mathbf{D}_{ei} : \mathbf{M}_{ei}^{(2)}) \times \right. \\ \left. \times [\mathbf{U} : ({}^{(1)}\mathbf{A}_{ej}^{(2)} + {}^{(2)}\mathbf{A}_{ej}^{(1)}) \cdot \mathbf{M}_{ej}^{(1)}] r_{ij}^{-8} \right\rangle. \quad (77)$$

The above contributions attract our attention because they involve the first power of the tensors ${}^{(1)}\mathbf{A}_e^{(2)}$ and ${}^{(2)}\mathbf{A}_e^{(1)}$ and not their product, as it is the case for the contribution (2a).

On inserting (19) into (56a) one obtains by (40a) for the two-body contributions (Kielich 1965b)

$${}_2S_{01(1)}^{\text{is}} = \frac{1}{kT} \sum_{n=1}^{\infty} \sum_{u=1}^{\infty} \frac{2^{n+u} (n!u!)^2 (2n+2u)!}{(2n)! (2n+1)! (2u)! (2u+1)!} \cdot \\ \cdot \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* \{ (\mathbf{U} : {}^{(1)}\mathbf{B}_{eei}^{(1+n)} [n] \mathbf{M}_{ei}^{(n)}) (\mathbf{M}_{ej}^{(u)} [u] \mathbf{M}_{ej}^{(u)} + \right. \\ \left. + (\mathbf{M}_{ei}^{(u)} [u] \mathbf{M}_{ei}^{(u)}) (\mathbf{U} : {}^{(1)}\mathbf{B}_{eej}^{(1+n)} [n] \mathbf{M}_{ej}^{(n)}) \} r_{ij}^{-2(n+u+1)} \right\rangle. \quad (78)$$

On expanding this general expression to within the term in quadrupole moments we have

$${}_2S_{01(1)}^{\text{is}} = \frac{2}{3kT} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* \{ [(\mathbf{U} : {}^{(1)}\mathbf{B}_{eei}^{(1+1)} \cdot \mathbf{M}_{ei}^{(1)}) (\mathbf{M}_{ej}^{(1)} \cdot \mathbf{M}_{ej}^{(1)}) \right. \\ + (\mathbf{M}_{ei}^{(1)} \cdot \mathbf{M}_{ei}^{(1)}) (\mathbf{U} : {}^{(1)}\mathbf{B}_{eej}^{(1+1)} \cdot \mathbf{M}_{ej}^{(1)})] r_{ij}^{-6} + \\ + [(\mathbf{U} : {}^{(1)}\mathbf{B}_{eei}^{(1+1)} \cdot \mathbf{M}_{ei}^{(1)}) (\mathbf{M}_{ej}^{(2)} : \mathbf{M}_{ej}^{(2)}) + \\ + (\mathbf{M}_{ei}^{(2)} : \mathbf{M}_{ei}^{(2)}) (\mathbf{U} : {}^{(1)}\mathbf{B}_{eej}^{(1+1)} \cdot \mathbf{M}_{ej}^{(1)}) + (\mathbf{U} : {}^{(1)}\mathbf{B}_{eei}^{(1+2)} : \mathbf{M}_{ei}^{(2)}) (\mathbf{M}_{ej}^{(1)} \cdot \mathbf{M}_{ej}^{(1)}) + \\ + (\mathbf{M}_{ei}^{(1)} \cdot \mathbf{M}_{ei}^{(1)}) (\mathbf{U} : {}^{(1)}\mathbf{B}_{eej}^{(1+2)} : \mathbf{M}_{ej}^{(2)})] r_{ij}^{-8} + \\ + \frac{28}{5} [(\mathbf{U} : {}^{(1)}\mathbf{B}_{eei}^{(1+2)} : \mathbf{M}_{ei}^{(2)}) (\mathbf{M}_{ej}^{(2)} : \mathbf{M}_{ej}^{(2)}) + \\ + (\mathbf{M}_{ei}^{(2)} : \mathbf{M}_{ei}^{(2)}) (\mathbf{U} : {}^{(1)}\mathbf{B}_{eej}^{(1+2)} : \mathbf{M}_{ej}^{(2)})] r_{ij}^{-10} \} \right\rangle. \quad (78a)$$

In a similar way we can calculate some other contributions to S_p^{is} , also dependent on r^{-p} for $p \geq 2$ (Kielich 1960b).

Application to anisotropic (depolarized) scattering

1 Zeroth approximation of the theory

In the zeroth approximation the polarizability tensor of a microsystem is independent of the electric field of the surrounding, neighbouring microsystems, and the anisotropic scattering constant (54) becomes

where the deviator defined by (71a) differs from zero only if the molecule is, intrinsically, optically anisotropic.

In the absence of interference effects we obtain immediately from (79) for the incoherent and coherent parts of the anisotropic scattering constant

$$S_{0,inc}^{anis} = \sum_{i=1}^N \mathbf{D}_{ei}^* : \mathbf{D}_{ei} = 6 \sum_{i=1}^N |A_{ei}|^2 \kappa_i^2, \quad (79a)$$

$$S_{0,coh}^{anis} = \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \mathbf{D}_{ei}^* : \mathbf{D}_{ej} \right\rangle, \quad (79b)$$

where

$$\kappa_i^2 = \frac{\mathbf{D}_{ei}^* : \mathbf{D}_{ei}}{6|A_{ei}|^2}, \quad (80)$$

is the parameter of optical anisotropy polarizability of the i th molecule.

The expressions of (79) and (80) are valid for any molecular symmetry, whereas they undergo considerable simplification if the scattering molecules are assumed to possess the axial symmetry:

$$S_{0,coh}^{anis} = 3 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N A_{ei}^* A_{ej} \kappa_i \kappa_j (3 \cos^2 \Theta_{ij} - 1) \right\rangle \quad (81)$$

with Θ_{ij} denoting the angle between the axes of symmetry of two mutually interacting molecules having the orientations Ω_i and Ω_j .

Obviously, in the absence of molecular interactions, the coherent scattering constants (79b) and (81) vanish.

For molecules of the same species (81) reduces to the well-known result

$$S_0^{anis} = S_{0,inc}^{anis} J_A, \quad (81a)$$

where

$$S_{0,inc}^{anis} = 6N|A_e|^2 \kappa^2,$$

and

$$J_A = \frac{1}{2} \rho \iint (3 \cos^2 \Theta_{12} - 1) g^{(2)}(r_{12}, \Omega_1, \Omega_2) d\mathbf{r}_{12} d\Omega_1 d\Omega_2 \quad (82)$$

is the angular molecular pair correlation parameter.

The influence of various angular molecular correlations (dispersional, electrostatic, inductional, etc.) on anisotropic light scattering has been discussed by many authors (Benoit and Stockmayer 1956; Kielich 1960a, 1967, 1968b; Pecora and Steele 1965; Kielich and Woźniak 1974; Woźniak and Kielich 1975; Gray and Gubbins 1975; Høye and Stell 1977; Ladanyi *et al* 1980). On the other hand, the parameter (82) accounting for these correlations is accessible to determination from experimental data (Deželić 1966; Kasprowicz and Kielich 1968; Lalanne 1969; Fechner 1969; Lucas and Jackson 1971; Kielich *et al* 1972; Alms *et al* 1974; Wróś 1975; Tancrede *et al* 1977a, b; Bertucci *et al* 1977; Battaglia *et al* 1979; Madden *et al* 1980; Vereshchagin 1980).

$$S_{01}^{\text{anis}} = - \left\langle \sum_{i=1}^N \sum_{j=1}^N \sum_{k \neq j}^N \mathbf{D}_{ei}^* : (\mathbf{A}_{ej} \cdot {}^{(1)}\mathbf{T}_{jk}^{(1)} \cdot \mathbf{A}_{ek}) \exp(i\Delta \mathbf{k} \cdot \mathbf{r}_{ij}) \right\rangle. \quad (83)$$

For molecules possessing the axial symmetry (83) yields for two-body contributions (Kielich 1971a; Kielich and Woźniak 1974)

$$S_{01}^{\text{anis}} = 3 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \{ 2A_{ei}^* A_{ej} \kappa_i (1 - \kappa_j) [A_{ei}(1 + \kappa_i) - A_{ej} \kappa_j] (3 \cos^2 \Theta_i - 1) r_{ij}^{-3} + 2A_{ei}^* A_{ej} \kappa_i \kappa_j [A_{ei}(1 + \kappa_i) + A_{ej}(1 + \kappa_j)] (3 \cos \theta_i \cos \theta_j \cos \Theta_{ij} - \cos^2 \Theta_{ij}) r_{ij}^{-3} \} \right\rangle, \quad (83a)$$

where θ_i and θ_j denote the angles between the symmetry axes of molecules i or j and the vector $\mathbf{r}_{ij}$. The three-body contribution is calculated in the paper of Kielich and Woźniak (1974).

In the case of a one-component system, (83a) reduces to

$$S_{01}^{\text{anis}} = 12A_e^3 \kappa N \{ (1 - \kappa) J_{RA} + 2\kappa(1 + \kappa) K_{RA} \}, \quad (83b)$$

where the radial-angular binary correlation parameters (Kielich 1971a)

$$J_{RA} = \frac{1}{2} \rho \iint (3 \cos^2 \Theta_1 - 1) r_{12}^{-3} g^{(2)}(r_{12}, \Omega_1, \Omega_2) d\mathbf{r}_{12} d\Omega_1 d\Omega_2, \\ K_{RA} = \frac{1}{2} \rho \iint (3 \cos \Theta_1 \cos \Theta_2 \cos \Theta_{12} - \cos^2 \Theta_{12}) \times \\ \times r_{12}^{-3} g^{(2)}(r_{12}, \Omega_1, \Omega_2) d\mathbf{r}_{12} d\Omega_1 d\Omega_2 \quad (84)$$

have been calculated for special molecular models (Kielich *et al* 1972; Woźniak and Kielich 1975). Obviously, the above parameters are defined so as to vanish in the absence of angular correlations.

Similarly to (77), we obtain for the dipole-quadrupole approximation (Kielich 1980):

$${}_2S_{01(1)}^{\text{anis}} = - \frac{2}{5kT} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \{ [\mathbf{D}_{ei}^* : (\mathbf{A}_{ei} \cdot \mathbf{M}_{ei}^{(2)})] [\mathbf{U} : ({}^{(1)}\mathbf{A}_{ej}^{(2)} + {}^{(2)}\mathbf{A}_{ej}^{(1)}) \cdot \mathbf{M}_{ej}^{(1)}] + [\mathbf{D}_{ei}^* : ({}^{(1)}\mathbf{A}_{ei}^{(2)} + {}^{(2)}\mathbf{A}_{ei}^{(1)}) \cdot \mathbf{M}_{ei}^{(1)}] \times \\ \times (\mathbf{D}_{ej} : \mathbf{M}_{ej}^{(2)}) \} r_{ij}^{-8} \right\rangle. \quad (85)$$

By (40a) and (19) we obtain for dipolar nonlinearly polarizable molecules (Kielich 1960b, 1968a):

$${}_2S_{01(1)}^{\text{anis}} = \frac{2}{75kT} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \{ (\mathbf{M}_{ei}^{(1)} \cdot \mathbf{D}_{ei}^* \cdot \mathbf{M}_{ei}^{(1)}) (\mathbf{U} : {}^{(1)}\mathbf{B}_{eej}^{(1+1)} \cdot \mathbf{M}_{ej}^{(1)}) + 25(\mathbf{D}_{ei}^* : {}^{(1)}\mathbf{B}_{eei}^{(1+1)} \cdot \mathbf{M}_{ei}^{(1)}) (\mathbf{M}_{ej}^{(1)} \cdot \mathbf{M}_{ej}^{(1)}) \} r_{ij}^{-6} \right\rangle. \quad (85a)$$

Analogous calculations, somewhat less complicated, can be carried out for other models of correlating polar molecules (Kielich 1960b, 1968a, b; Kielich and Woźniak 1974; Woźniak and Kielich 1975; Frenkel and McTague 1980).

8.3 Second approximation of the theory

8.3a. *Contribution from linear multipole polarizabilities:* We shall now proceed a step further, and shall take into account the Yvon–Kirkwood translational fluctuation effect for molecules with intrinsic anisotropy. We obtain, by (36) and (37) in the electric dipole approximation for the two-body contribution:

$$\begin{aligned}
 {}_2S_{11}^{\text{anis}} &= \left\langle \sum_{i=1}^N \sum_{j=1}^N \left\{ 12 |A_{ei} A_{ej}|^2 + \frac{7}{5} [|A_{ei}|^2 (\mathbf{D}_{ej}^* : \mathbf{D}_{ej}) + \right. \right. \\
 &\quad \left. \left. + (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) |A_{ej}|^2 \right] + \frac{22}{25} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) (\mathbf{D}_{ej}^* : \mathbf{D}_{ej}) \right\} r_{ij}^{-6} \right\rangle, \\
 {}_2S_{02}^{\text{anis}} &= \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \left\{ 2 [\mathbf{D}_{ei}^* : (\mathbf{D}_{ei} \cdot \mathbf{D}_{ei}) + 2 A_{ei} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei})] A_{ej} + \right. \right. \\
 &\quad \left. \left. + \frac{1}{5} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) A_{ej}^2 + \frac{1}{150} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) (\mathbf{D}_{ej}^* : \mathbf{D}_{ej}) \right\} r_{ij}^{-6} \right\rangle. \quad (86)
 \end{aligned}$$

Similarly, we have for the three-body contribution

$$\begin{aligned}
 {}_3S_{11}^{\text{anis}} &= 12 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N (A_{ei}^* A_{ek} + A_{ei} A_{ek}^*) [|A_{ej}|^2 + \right. \\
 &\quad \left. + \frac{7}{60} (\mathbf{D}_{ej}^* : \mathbf{D}_{ej})] r_{ij}^{-3} r_{jk}^{-3} P_2 \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) \right\rangle, \\
 {}_3S_{02}^{\text{anis}} &= \frac{1}{5} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N \left\{ 20 (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) A_{ej} + A_{ei} (\mathbf{D}_{ej}^* : \mathbf{D}_{ej}) \right\} A_{ek} \times \right. \\
 &\quad \left. \times r_{ij}^{-3} r_{jk}^{-3} P_2 \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) \right\rangle, \quad (87)
 \end{aligned}$$

and for the four-body contribution

$$\begin{aligned}
 {}_4S_{11}^{\text{anis}} &= 6 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N \sum_{l \neq k \neq j \neq i}^N A_{ei}^* A_{ej} A_{ek}^* A_{el} \times \right. \\
 &\quad \left. \times r_{ij}^{-3} r_{jl}^{-3} P_2 \left(\frac{\mathbf{r}_{ik} \cdot \mathbf{r}_{jl}}{r_{ik} r_{jl}} \right) \right\rangle, \quad (88a)
 \end{aligned}$$

$${}_4S_{02}^{\text{anis}} = 0. \quad (88b)$$

On addition of (86) and (87) as well as the respective contributions ${}_2S_{20}^{\text{anis}}$ and ${}_3S_{20}^{\text{anis}}$ we obtain the previously derived results for $S_{02}^{\text{anis}} + S_{11}^{\text{anis}} + S_{20}^{\text{anis}}$ (Kielich 1968a, equations (2.4.12)).

$$\begin{aligned}
{}_2S_{11}^{\text{anis}} &= 6 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N |A_{ei} A_{ej}|^2 \left\{ 2 + \frac{7}{5} (\kappa_i^2 + \kappa_j^2) + \frac{132}{25} \kappa_i^2 \kappa_j^2 \right\} r_{ij}^{-6} \right\rangle, \\
{}_2S_{02}^{\text{anis}} &= \frac{6}{5} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N |A_{ei}|^2 \{ (20 A_{ei} + A_{ej}) A_{ej} \kappa_i^2 + \right. \\
&\quad \left. + 10 A_{ei} A_{ej} \kappa_i^3 + \frac{1}{5} A_{ej}^2 \kappa_i^2 \kappa_j^2 \} r_{ij}^{-6} \right\rangle, \tag{86a}
\end{aligned}$$

$$\begin{aligned}
{}_3S_{11}^{\text{anis}} &= 12 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N (A_{ei}^* A_{ek} + A_{ei} A_{ek}^*) |A_{ej}|^2 \times \right. \\
&\quad \times \left(1 + \frac{7}{10} \kappa_j^2 \right) r_{ij}^{-3} r_{jk}^{-3} P_2 \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) \Bigg\rangle, \\
{}_3S_{02}^{\text{anis}} &= \frac{6}{5} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N \{ 20 |A_{ei}|^2 A_{ej} \kappa_i^2 + A_{ei} |A_{ej}|^2 \kappa_j^2 \cdot \right. \\
&\quad \cdot r_{ij}^{-3} r_{jk}^{-3} P_2 \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) \Bigg\rangle. \tag{87a}
\end{aligned}$$

The contributions (86a) and (87a) jointly give the results derived by Kielich (1968a) for liquid mixtures. Applied to one-component fluids, they give the formulae evaluated numerically by Woźniak and Kielich (1975).

Recently, Cox and Madden (1980), applying the spherical tensor method, have calculated the contributions S_{11}^{is} and S_{11}^{anis} only, for the case of a one-component fluid. Their formulae, compared with those resulting from (72a) and (72b) for S_{11}^{is} and (88), (86a) and (87a) for S_{11}^{anis} , as applied to molecules having identical real polarizabilities $\alpha = A_i = A_j = A_k$ and anisotropies $\gamma = 3A_i \kappa_i = 3A_j \kappa_j = A_{\parallel} - A_{\perp}$, are found to differ only in numerical factors at the term $\gamma^4 = (3AK)^4$. Obviously, for weakly optically anisotropic molecules, this term is of no relevance.

Taking into account the terms with dipole-quadrupole polarizability in the expansions (36) and (57) we arrive at the following binary and ternary contributions (Kielich 1980):

$${}_2S_{11}^{\text{anis}} = \frac{16}{7} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \{ |A_{ei}|^2 P_j^{(3,3)} + \frac{73}{90} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) Q_j^{(3,3)} \} r_{ij}^{-8} \right\rangle, \tag{89a}$$

$${}_2S_{02}^{\text{anis}} = 2 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \{ \mathbf{D}_{ei}^* : ({}^{(1)}\mathbf{A}_{ei}^{(2)} : {}^{(2)}\mathbf{A}_{ei}^{(1)}) A_{ej} + \frac{1}{105} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) W_j^{(3,3)} \} r_{ij}^{-8} \right\rangle, \tag{89b}$$

$${}_3S_{11}^{\text{anis}} = \frac{-16}{7} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N A_{ei}^* P_j^{(3,3)} A_{ek} r_{ij}^{-4} r_{jk}^{-4} P_3 \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) \right\rangle, \tag{89c}$$

where the molecular parameters $P_j^{(3,3)}$, $Q_j^{(3,3)}$ and $W_j^{(3,3)}$ are given by appropriate combinations of products of the tensors ${}^{(1)}\mathbf{A}_{ej}^{(2)}$ and ${}^{(2)}\mathbf{A}_{ej}^{(1)}$.

For tetrahedrally-symmetric molecules (*e.g.* CH_4) we have:

$$G_j^{(3,3)} = K_j^{(3,3)} = P_j^{(3,3)} = Q_j^{(3,3)} = W_j^{(3,3)} = 6(A_{xyz}^{(j)})^2,$$

raise the two-body interaction contributions (72f) and (89a). It is also of interest that the cross contributions (69c) and (89b) are non-zero only for two-body interactions; thus, they can play an important role if (72f) and (72g), as well (89a) and (89c), cancel out mutually.

In the case of anisotropic axially-symmetric molecules of one species (*e.g.* CO₂), (72b) and (39a) lead to the recent results of Amos *et al* (1980) for the binary collision-induced Raman scattering.

If the terms with the quadrupole-quadrupole polarizability tensor $^{(2)}\mathbf{A}_i^{(2)}$ are taken into account in the expansion (37), one obtains by (55b) for two- and three-body interactions (Kielich 1980):

$$\begin{aligned} {}_2S_{02}^{\text{anis}} &= \frac{4}{7} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \left\{ |A_{ei}|^2 + \frac{1}{30} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) [(\mathbf{D}_{ej}^* : ^{(2)}\mathbf{A}_{ej}^{(2)}) : \mathbf{U}] + \right. \right. \\ &\quad \left. \left. + \frac{35}{6} [\mathbf{D}_{ei}^* : (\mathbf{D}_{ei} \cdot \mathbf{D}_{ei}) + 2A_{ei}^* (\mathbf{D}_{ei} : \mathbf{D}_{ei})] A_{ej}^4 \right\} r_{ij}^{-8} \right\rangle, \\ {}_3S_{02}^{\text{anis}} &= -\frac{4}{7} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq j \neq i}^N \left\{ A_{ei}^* [(\mathbf{D}_{ei} : ^{(2)}\mathbf{A}_{ei}^{(2)}) : \mathbf{U}] + \right. \right. \\ &\quad \left. \left. + \frac{35}{3} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) A_{ej}^{(4)} \right\} r_{ij}^{-4} r_{jk}^{-4} P_3 \left(\frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jk}}{r_{ij} r_{jk}} \right) \right\rangle. \end{aligned} \quad (90)$$

8.3b Contributions from nonlinear multipole polarizabilities: For nonlinearly polarizable molecules with an intrinsic dipole moment $\mathbf{M}_{ei}^{(1)}$ the first approximation of (40a) leads to previously calculated results for S_{11} (Kielich 1960b, 1968a); however, the second approximation of (40b) yields the following two-body contribution (Kielich 1980):

$$\begin{aligned} {}_2S_{02}^{\text{anis}} &= 2 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \left\{ A_{ei}^* (\mathbf{D}_{ei} : ^{(1)}\mathbf{B}_{eei}^{(1+1)} \cdot \mathbf{M}_{ei}^{(1)}) + \right. \right. \\ &\quad \left. \left. + \frac{1}{225} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) (\mathbf{U} : ^{(1)}\mathbf{B}_{eej}^{(1+1)} \cdot \mathbf{M}_{ej}^{(1)}) \right\} r_{ij}^{-6} \right\rangle. \end{aligned} \quad (91)$$

For molecules having an intrinsic quadrupole moment $\mathbf{M}_{ei}^{(2)}$ and the nonlinear dipole-quadrupole polarizability $^{(1)}\mathbf{B}_{eei}^{(1+2)}$, (40a), (40b) lead, in the two-body approximation (Kielich 1980), to

$$\begin{aligned} {}_2S_{11}^{\text{anis}} &= \frac{56}{135} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \left\{ [3 ^{(1)}\mathbf{B}_{eei}^{(1+2)*} : ^{(1)}\mathbf{B}_{eei}^{(1+2)} - \right. \right. \\ &\quad \left. \left. - (\mathbf{U} : ^{(1)}\mathbf{B}_{eei}^{(1+2)*} : (\mathbf{U} : ^{(1)}\mathbf{B}_{eei}^{(1+2)})] (\mathbf{M}_{ej}^{(2)} : \mathbf{M}_{ej}^{(2)}) + \right. \right. \\ &\quad \left. \left. + \frac{8}{49} [(3\mathbf{U}_{13} : ^{(1)}\mathbf{B}_{eei}^{(1+2)} - \mathbf{U}_{12} : ^{(1)}\mathbf{B}_{eei}^{(1+2)*} : \mathbf{M}_{ei}^{(2)})] [(3\mathbf{U}_{13} : ^{(1)}\mathbf{B}_{eej}^{(1+2)} - \right. \right. \\ &\quad \left. \left. - \mathbf{U}_{12} : ^{(1)}\mathbf{B}_{eej}^{(1+2)}) : \mathbf{M}_{ej}^{(2)}] \right\} r_{ij}^{-10} \right\rangle, \\ {}_2S_{02}^{\text{anis}} &= 2 \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \left\{ A_{ei}^* (\mathbf{D}_{ej} : ^{(1)}\mathbf{B}_{eej}^{(1+2)} : \mathbf{M}_{ej}^{(2)}) + \frac{1}{315} (\mathbf{D}_{ei}^* : \mathbf{D}_{ei}) \times \right. \right. \\ &\quad \left. \left. \times (3\mathbf{U}_{13} : ^{(1)}\mathbf{B}_{eej}^{(1+2)} - \mathbf{U}_{12} : ^{(1)}\mathbf{B}_{eej}^{(1+2)}) : \mathbf{M}_{ej}^{(2)} \right\} r_{ij}^{-8} \right\rangle. \end{aligned} \quad (92)$$

By the expansion (42), similar calculations yield successively for the two-body contribution from interaction between an intrinsic dipole or quadrupole moment and induced third-order dipole moment (Kielich 1960b, 1968a):

$${}_2S_{02}^{\text{anis}} = \frac{1}{13} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \{ C_{ei}^{(4)} (\mathbf{M}_{ej}^{(1)} \cdot \mathbf{D}_{ej}^* \cdot \mathbf{M}_{ej}^{(1)}) + \right. \\ \left. + 5 (\mathbf{D}_{ei}^* : {}^{(1)}_e C_{eeei}^{(1+1+1)} : \mathbf{U}) (\mathbf{M}_{ej}^{(1)} : \mathbf{M}_{ej}^{(1)}) \} r_{ij}^{-6} \right\rangle, \quad (93)$$

$${}_2S_{02}^{\text{anis}} = \frac{1}{21} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \{ 20 C_{ei}^{(4)} [\mathbf{D}_{ej}^* : (\mathbf{M}_{ej}^{(2)} : \mathbf{M}_{ej}^{(2)})] + \right. \\ \left. + 7 (\mathbf{D}_{ei}^* : {}^{(1)}_e C_{eeei}^{(1+1+1)} : \mathbf{U}) (\mathbf{M}_{ej}^{(2)} : \mathbf{M}_{ej}^{(2)}) \} r_{ij}^{-8} \right\rangle. \quad (94)$$

9. Linewidth broadening in quasi-elastic scattering by correlated microsystems

This section is aimed at presenting a stochastic treatment of the spectral distribution of light scattered by systems of atoms and molecules, correlated in time and space.

9.1 Time-correlations intensity of scattered light

Similarly to the integral intensity of scattered light (50) we can introduce the following time-correlation intensity of scattered light (for processes stationary in time)

$$I_{e_i}(\mathbf{r}, t) = \frac{R_e^2(\omega_s)}{8\pi c^3} \left\langle \sum_{i=1}^N \sum_{j=1}^N \mathbf{e}_s \cdot \ddot{\mathbf{Z}}(t_i) * \ddot{\mathbf{Z}}(t_j + t) \cdot \mathbf{e}_s^* \right\rangle. \quad (95)$$

With regard to the theorem of Wiener and Khinchin, the Fourier transform of the time-correlation intensity (95) determines the spectral density

$$S_{e_i}(\Delta \mathbf{k}, \omega) = (2\pi)^{-4} \int \int_{-\infty}^{+\infty} I_{e_i}(\mathbf{r}, t) \exp[i(\omega_s t - \Delta \mathbf{k} \cdot \mathbf{r})] dt d\vec{\mathbf{r}}. \quad (95a)$$

The range of applicability of this theorem to time-dependent spectral processes has been the subject of an analysis by Eberly and Wódkiewicz (1977).

Restricting the problem to electric-dipole scattering in the wave zone, we write (95) in the form

$$I_{e_e}(\mathbf{r}, t) = Q(\omega_s) I_0(\mathbf{r}, t) \left\langle \sum_{i=1}^N \sum_{j=1}^N [\mathbf{e}_s \cdot \boldsymbol{\Pi}_e(\mathbf{r}_i^0, \Omega_i^0) * \mathbf{e}^*] \times \right. \\ \left. \times [\mathbf{e}_s^* \cdot \boldsymbol{\Pi}_e(\mathbf{r}_j^t, \Omega_j^t) \cdot \mathbf{e}] \exp[i\Delta \mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \right\rangle, \quad (96)$$

where the position and orientation of a microsystem i is given at the moment of time t by the variables $\mathbf{r}_i^t$ and Ω_i^t , and

$$I_0(\mathbf{r}, t) = I_0 \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)].$$

On decomposing the effective polarizability tensor $\Pi(\mathbf{r}, \Omega)$ into three irreducible tensors and on averaging in (96) over all possible orientations of the microsystems, we obtain respectively for isotropic, antisymmetric and anisotropic scattering (Kielich *et al* 1981)

$$I_{e,e}^{(0)}(\mathbf{r}, t) = \frac{1}{3} Q(\omega_s) I_0(\mathbf{r}, t) S^{(0)}(\Delta\mathbf{k}, t) |\mathbf{e}_s \cdot \mathbf{e}^*|^2, \quad (96a)$$

$$I_{e,e}^{(1)}(\mathbf{r}, t) = \frac{1}{6} Q(\omega_s) I_0(\mathbf{r}, t) S^{(1)}(\Delta\mathbf{k}, t) (1 - |\mathbf{e}_s \cdot \mathbf{e}|^2), \quad (96b)$$

$$I_{e,e}^{(2)}(\mathbf{r}, t) = \frac{1}{30} Q(\omega_s) I_0(\mathbf{r}, t) S^{(2)}(\Delta\mathbf{k}, t) (3 + 3|\mathbf{e}_s \cdot \mathbf{e}|^2 - 2|\mathbf{e}_s \cdot \mathbf{e}^*|^2). \quad (96c)$$

Above, we have introduced the time-dependent correlation functions ($h = 0, 1, 2$)

$$S^{(h)}(\Delta\mathbf{k}, t) = \left\langle \sum_{i=1}^N \sum_{j=1}^N \mathbf{\Pi}_e^{(h)}(\mathbf{r}_i^0, \Omega_i^0)^* : \mathbf{\Pi}_e^{(h)}(\mathbf{r}_j^t, \Omega_j^t) \exp[i\Delta\mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \right\rangle \quad (97)$$

characterizing the molecular-statistical dynamics of isotropic ($h = 0$), antisymmetric ($h = 1$) and anisotropic ($h = 2$) scattering.

9.2 Correlated molecules without change of polarizability

If the molecules are correlated statistically but if we neglect the changes in their polarizabilities caused by the molecular fields (the zeroth approximation), we obtain from (97)

$$S^{(h)}(\Delta\mathbf{k}, t) = \left\langle \sum_{i=1}^N \sum_{j=1}^N \mathbf{A}_e^{(h)}(\Omega_i^0)^* : \mathbf{A}_e^{(h)}(\Omega_j^t) \exp[i\Delta\mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \right\rangle. \quad (98)$$

In particular, for anisotropic scattering, we get:

$$S^{(2)}(\Delta\mathbf{k}, t) = \left\langle \sum_{i=1}^N \sum_{j=1}^N \mathbf{D}_e(\Omega_i^0)^* : \mathbf{D}_e(\Omega_j^t) \exp[i\Delta\mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \right\rangle. \quad (98a)$$

9.2a Correlation function of isotropic scattering: In the case of atoms and isotropically polarizable molecules we have by (98) isotropic scattering only, with the correlation function

$$S^{(0)}(\Delta\mathbf{k}, t) = 3 \left\langle \sum_{i=1}^N \sum_{j=1}^N A_{ei}^* A_{ej} \exp[i\Delta\mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \right\rangle \quad (99)$$

which, for like correlating microsystems, reduces to

$$S^{(0)}(\Delta\mathbf{k}, t) = 3N |A_e|^2 F(\Delta\mathbf{k}, t). \quad (99a)$$

Here, we have introduced the well known intermediate scattering correlation function

$$F(\Delta\mathbf{k}, t) = N^{-1} \left\langle \sum_{i=1}^N \sum_{j=1}^N \exp[i\Delta\mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \right\rangle \quad (100)$$

discussed in the theory of neutron scattering.

After Van Hove (1954), we introduce the space-time binary correlation function

$$G^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t) = G_s(\mathbf{r}_i^0, \mathbf{r}_j^t, t) + G_D(\mathbf{r}_i^0, \mathbf{r}_j^t, t), \quad (101)$$

$G_D(\mathbf{r}_i^0, \mathbf{r}_j^t, t)$ expresses the probability of finding a molecule j at the point $\mathbf{r}_j^t$ if the fixed molecule i was at $\mathbf{r}_i^0$ at $t = 0$.

By having recourse to the Van Hove function (101) we can split (100) into two parts (see Powles 1973), a self-correlation part, describing incoherent scattering

$$F_{\text{inc}}(\Delta \mathbf{k}, t) = V^{-1} \int \int \exp[i\Delta \mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_i^t)] G_S(\mathbf{r}_i^0, \mathbf{r}_i^t, t) d\mathbf{r}_i^0 d\mathbf{r}_i^t \quad (100a)$$

and a distinct part, describing coherent scattering on stochastically correlated molecules

$$F_{\text{coh}}(\Delta \mathbf{k}, t) = \frac{\rho}{V} \int \int \exp[i\Delta \mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] G_D(\mathbf{r}_i^0, \mathbf{r}_j^t, t) d\mathbf{r}_i^0 d\mathbf{r}_j^t. \quad (100b)$$

It is important to find a reasonable and physically plausible analytical construction of G_S and—especially— G_D . Here, of essential interest to us is the interval of intermediate times of molecular relaxations ($10^{-13} < t < 10^{-6}$ sec), for which one may apply the solution on the model of diffusion of translational or rotational molecular motion.

On the assumption of the Einstein–Smoluchowski free translational model, we have

$$G_S(\mathbf{r}_i^0, \mathbf{r}_i^t, t) = (4\pi D_T t)^{-3/2} \exp(-|\mathbf{r}_i^t - \mathbf{r}_i^0|^2 / 4D_T t). \quad (102)$$

Thus, the incoherent scattering function (100a) finally takes the form

$$F_{\text{inc}}(\Delta \mathbf{k}, t) = \exp(-|\Delta \mathbf{k}|^2 D_T t), \quad (103)$$

where D_T is the coefficient of translational diffusion of Brownian particles.

The calculation of the coherent scattering function (100b) is by no means simple for a lack of the analytical form of the distinct correlation function G_D . In some cases use can be made of Vineyard's (1958) convolution approximation

$$G_D(\mathbf{r}_i^0, \mathbf{r}_j^t, t) = \int g^{(2)}(\mathbf{r}_{ij}^0) G_S(\mathbf{r}_j^0, \mathbf{r}_j^t, t) d\mathbf{r}_j^0 \quad (104)$$

and we reduce the coherent scattering function (100b) to the following form (see *e.g.* Nijboer and Rahman 1966):

$$F_{\text{coh}}(\Delta \mathbf{k}, t) = \Gamma_{00}^0(\Delta \mathbf{k}) F_{\text{inc}}(\Delta \mathbf{k}, t), \quad (105)$$

where the integral parameter $\Gamma_{00}^0(\Delta \mathbf{k})$ is given by (66).

By (99a), (103) and (105) we can write finally

$$S^{(0)}(\Delta \mathbf{k}, t) = 3N |A_e|^2 F_{\text{inc}}(\Delta \mathbf{k}, t) [1 + \Gamma_{00}^0(\Delta \mathbf{k})]. \quad (106)$$

9.2b Correlation functions of antisymmetric and anisotropic scattering: In the case of anisotropic molecules we have to replace the Van Hove function (101) by the generalized space-time correlation functions;

$$G^{(2)}(\mathbf{r}_1, \Omega_1^0, \mathbf{r}_2, \Omega_2^0, t) = G_S(\mathbf{r}_i^0, \Omega_i^0; \mathbf{r}_i^t, \Omega_i^t, t) + G_D(\mathbf{r}_i^0, \Omega_i^0; \mathbf{r}_j^t, \Omega_j^t, t). \quad (107)$$

involving additionally the molecular orientation variables Ω_i and Ω_j .

Regrettably, as yet, not much is known concerning the analytical form of (28) and hardly anything concerning G_D (Rowlinson and Evans 1975; Evans 1977; Williams

1978). We now proceed to introduce certain model assumptions to simplify our further calculations:

(i) the translational and rotational motions of the molecules are mutually independent,

(ii) after Vineyard (1958), the molecules interact with one another at the moment of time $t = 0$ only, whereas at $t > 0$ they are statistically independent and move in conformity with the laws of self-diffusion.

With the above assumptions and applying a procedure due to Steele and Pecora (1965), one can expand (107) in a series in spherical Wigner functions $D_{KM}^J(\Omega)$:

$$G_S(\mathbf{r}_i^0, \Omega_i^0; \mathbf{r}_i^t, \Omega_i^t, t) = \sum_{JKMM'} f_{MM'}^J(\mathbf{r}_{ii}^t, t) \bar{D}_{KM}^J(\Omega_i^0) \bar{D}_{KM'}^J(\Omega_i^t)^*, \quad (107a)$$

$$G_D(\mathbf{r}_i^0, \Omega_i^0; \mathbf{r}_j^t, \Omega_j^t, t) = \sum_{J_i K_i M_i} \sum_{J_j K_j M_j} g_{K_i M_i, K_j M_j}^{J_i J_j}(\mathbf{r}_{ij}^t, t) \times \bar{D}_{K_i M_i}^{J_i}(\Omega_i^0) \bar{D}_{K_j M_j}^{J_j}(\Omega_j^t)^*, \quad (107b)$$

where

$$\bar{D}_{KM}^J(\Omega) = \left(\frac{2J+1}{\Omega} \right)^{1/2} D_{KM}^J(\Omega).$$

The analytical form of the functions

$$f_{MM'}^J(\mathbf{r}_{ii}^t, t) \quad \text{and} \quad g_{K_i M_i, K_j M_j}^{J_i J_j}(\mathbf{r}_{ij}^t, t)$$

can be specified for a given model of the molecular motions, the simplest model of this kind being that of translational-rotational diffusion. In this case we have

$$f_{MM'}^J(\mathbf{r}_{ii}^t, t) = \delta_{MM'} G_S(\mathbf{r}_i^0, \mathbf{r}_i^t, t) \exp(-t/\tau_M^J), \quad (108)$$

where $G_S(\mathbf{r}_i^0, \mathbf{r}_i^t, t)$ is given by (102) and τ_M^J denotes the M th component of the rotational relaxation time of the J th order which, for symmetric top molecules, is given by

$$\tau_M^J = \{ J(J+1)D_{11}^R + M^2(D_{33}^R - D_{11}^R) \}^{-1} \quad (109)$$

D_{11}^R and D_{33}^R being the principal values of the rotational diffusion tensor.

The expansion coefficients of (108b) can be expressed as follows (Steele and Pecora 1965):

$$g_{K_i M_i, K_j M_j}^{J_i J_j}(\mathbf{r}_{ij}^t, t) = \exp(-t/\tau_M^J) \int g_{K_i M_i, K_j M_j}^{J_i J_j}(\mathbf{r}_{ij}^0) G_S(\mathbf{r}_j^0, \mathbf{r}_j^t, t) d\mathbf{r}_j^0. \quad (110)$$

Our problem becomes quite simple on transforming the Cartesian tensor $\mathbf{A}_e^{(h)}(\Omega)$ occurring in (98) to spherical representation and we obtain by (107)–(109) for the antisymmetric and anisotropic scattering functions (Knaust and Kielich 1979).

$$S^{(1)}(\Delta\mathbf{k}, t) = N F_{\text{inc}}(\Delta\mathbf{k}, t) \sum_{MM'} (A_{eM}^{(1)})^* A_{eM'}^{(1)} \exp(-t/\tau_M^1) [\delta_{MM'} + \Gamma_{MM'}^1(\Delta\mathbf{k})], \quad (111)$$

$$S^{(2)}(\Delta\mathbf{k}, t) = N F_{\text{inc}}(\Delta\mathbf{k}, t) \sum (A_{eM}^{(2)})^* A_{eM'}^{(2)} \exp(-t/\tau_M^2) [\delta_{MM'} + \Gamma_{MM'}^2(\Delta\mathbf{k})],$$

$$\Gamma'_{MM'}(\Delta \mathbf{k}) = \sum_N \frac{(-1)^{N-M}}{2J+1} \int_0^\infty g_{N,-M,-N,M'}^{JJ}(\mathbf{r}_{12}) \frac{\sin \Delta k r_{12}}{\Delta k r_{12}} d\mathbf{r}_{12}. \quad (113)$$

If $\Delta \mathbf{k} \cdot \mathbf{r} \ll 1$ (short-range correlation), (113) reduces to the Steele (1965) parameter

$$\Gamma'_{MM'}(0) = \sum_N \frac{(-1)^{N-M}}{2J+1} \int_0^\infty g_{N,-M,-N,M'}^{JJ}(r_{12}) d\mathbf{r}_{12}, \quad (113a)$$

which has been calculated numerically for concrete models of interacting molecules (see *e.g.* Kielich 1967, 1972; Ananth *et al* 1974; Woźniak and Kielich 1975; Høye and Stell 1977; Głaz 1981).

In the absence of molecular interactions, the parameters (113) vanish and the time correlation functions (111) and (112) describe incoherent antisymmetric and anisotropic light scattering

$$S_{\text{inc}}^{(1)}(\Delta \mathbf{k}, t) = N F_{\text{inc}}(\Delta \mathbf{k}, t) \sum_M |A_{eM}^{(1)}|^2 \exp(-t/\tau_M^1), \quad (111a)$$

$$S_{\text{inc}}^{(2)}(\Delta \mathbf{k}, t) = N F_{\text{inc}}(\Delta \mathbf{k}, t) \sum_M |A_{eM}^{(2)}|^2 \exp(-t/\tau_M^2). \quad (112a)$$

9.3 Contributions from multipole polarizabilities

The results of recent experimental and theoretical spectral studies are evidence of the importance of contributions from multipolar polarizabilities (see *e.g.* Kielich 1963, 1968; Pasmanter *et al* 1976; Buckingham and Tabisz 1978; Tabisz 1979; Posch 1979, 1980; Shelton and Tabisz 1980; Cox and Madden 1980; Amos *et al* 1980; Kielich *et al* 1981). These contributions bear on the anisotropic as well as the isotropic scattering, inherent in the time-correlation functions (97) and are determined with complete generality by the expressions derived for effective polarizabilities derived in §4. Since the latter, in spite of the compact Cartesian tensor notation applied, are rather complex mathematically, we shall restrict ourselves here to writing the lower-order contributions to the correlation function of isotropic scattering. By (97), it can be written explicitly in the form:

$$S^{(0)}(\Delta \mathbf{k}, t) = \frac{1}{3} \left\langle \sum_{i=1}^N \sum_{j=1}^N \{ \Pi_e(\mathbf{r}_i^0, \Omega_i^0) : \mathbf{U} \}^* \times \right. \\ \left. \times \{ \Pi_e(\mathbf{r}_j^t, \Omega_j^t) : \mathbf{U} \} \exp[i\Delta \mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \right\rangle \quad (114)$$

With regard to (36) we thus arrive at the following contributions from linear multipole polarizabilities (on neglecting magneto-electric terms):

$$S_{01}^{(0)}(\Delta \mathbf{k}, t) = \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{(-1)^{n_2}}{(2n_1-1)!!(2n_2-1)!!} \times \\ \times \left\langle \sum_{i=1}^N \sum_{j=1}^N \sum_{k \neq j}^N A_e^*(\Omega_i^0) \{ {}^{(1)}_e \mathbf{A}_e^{(n_1)}(\Omega_j^t) [n_1] {}^{(n_1)} \mathbf{T}_{jk}^{(n_2)} \} \times \right. \\ \left. \times [n_2] {}^{(n_2)}_e \mathbf{A}_e^{(1)}(\Omega_i^t) \} : \mathbf{U} \exp[i\Delta \mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \right\rangle, \quad (115)$$

$$\begin{aligned}
S_{11}^{(0)}(\Delta \mathbf{k}, t) = & \frac{1}{3} \sum_{n_1=1}^{\infty} \cdots \sum_{n_4=1}^{\infty} \frac{(-1)^{n_1+n_4}}{(2n_1-1)!! \cdots (2n_4-1)!!} \times \\
& \times \left\langle \sum_{i=1}^N \sum_{j=1}^N \sum_{k \neq i}^N \sum_{l \neq j}^N \{ {}^{(1)}_e \mathbf{A}_e^{(n_1)}(\Omega_i^0)[n_1] {}^{(n_1)}\mathbf{T}_{ik}^{(n_2)}[n_2] \times \right. \\
& \times {}^{(n_2)}_e \mathbf{A}_e^{(1)}(\Omega_k^0) \}^* : \mathbf{U} \{ {}^{(1)}_e \mathbf{A}_e^{(n_3)}(\Omega_j^t)[n_3] {}^{(n_3)}\mathbf{T}_{jl}^{(n_4)}[n_4] \times \\
& \times {}^{(n_4)}_e \mathbf{A}_e^{(1)}(\Omega_l^t) \} : \mathbf{U} \exp[i\Delta \mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \Bigg\rangle. \quad (116)
\end{aligned}$$

To derive the coherent contributions to (114) of the same order of magnitude one has to take into account, beside the currently considered contribution (116), moreover mixed contributions originating in the second-order change in the effective polarizability (37) (omitting magneto-electric terms):

$$\begin{aligned}
S_{02}^{(0)}(\Delta \mathbf{k}, t) = & \sum_{n_1=1}^{\infty} \cdots \sum_{n_4=1}^{\infty} \frac{(-1)^{n_2+n_4}}{(2n_1-1)!! \cdots (2n_4-1)!!} \times \\
& \times \left\langle \sum_{i=1}^N \sum_{j=1}^N \sum_{k \neq j}^N \sum_{l \neq k}^N A_e^*(\Omega_i^0) \{ {}^{(1)}_e \mathbf{A}_e^{(n_1)}(\Omega_j^t)[n_1] \times \right. \\
& \times {}^{(n_1)}\mathbf{T}_{jk}^{(n_2)}[n_2] {}^{(n_2)}_e \mathbf{A}_e^{(n_3)}(\Omega_k^t)[n_3] {}^{(n_3)}\mathbf{T}_{kl}^{(n_4)}[n_4] \times \\
& \times {}^{(n_4)}_e \mathbf{A}_e^{(1)}(\Omega_l^t) \} : \mathbf{U} \exp[i\Delta \mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \Bigg\rangle. \quad (117)
\end{aligned}$$

Obviously, the contribution $S_{20}^{(0)}(\Delta \mathbf{k}, t)$ is of a similar form.

All these contributions determine isotropic coherent light scattering and can be split in the standard manner into components due to two-, three- and four-body interactions. Obviously, in this way, the spectral distribution is determined by new angular correlation functions. The only complete to-the-end analyses are, hitherto, those of Bancewicz (1979, 1980) and Frenkel and McTague (1980) for axially symmetric molecules in the dipole-induced dipole approximation and of Posch (1980) for tetrahedral ones in the dipole-quadrupole approximation. A discussion of the angular correlation functions for higher dipole-quadrupole, quadrupole-quadrupole and dipole-octupole approximations has been given quite recently by Kielich *et al* (1981).

As in the case of integral scattering, an important role is played by contributions from nonlinear multipole polarizabilities in that of spectral scattering. As an example, we adduce the following first-order contribution which, by (40a) and (114), has the form

$$\begin{aligned}
S_{01}^{(0)}(\Delta \mathbf{k}, t) = & \frac{1}{2} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{(-1)^{n_2}}{(2n_1-1)!! (2n_2-1)!!} \times \\
& \times \left\langle \sum_{i=1}^N \sum_{j=1}^N \sum_{k \neq j}^N {}_e A_e^*(\Omega_i^0) \{ \mathbf{U} : {}^{(1)}_e \mathbf{B}_{ee}^{(1+n_1)}(\Omega_j^t) + \right. \\
& + {}^{(1)}_e \mathbf{B}_{ee}^{(n_1+1)}(\Omega_j^t) \} [n_1] {}^{(n_1)}\mathbf{T}_{jk}^{(n_2)}[n_2] \mathbf{M}_e^{(n_2)}(\Omega_k^t) \times \\
& \times \exp[i\Delta \mathbf{k} \cdot (\mathbf{r}_i^0 - \mathbf{r}_j^t)] \Bigg\rangle. \quad (118)
\end{aligned}$$

other contributions to (114) due to the nonlocal multipole polarizabilities.

Finally, it may be worth stressing that the correlation functions of isotropic scattering (115)–(118) and analogical functions of anisotropic light scattering (not given explicitly in this review) contain all multipolar contributions, readily adaptable to various molecular symmetries of the spherical top and symmetric top kind. On applying reasonable model assumptions their mathematical form simplifies considerably. Their numerical evaluation is easy to perform since, as stated above, the numerical values of the electric multipoles and nonlinear polarizabilities of many of the simpler molecules (see *e.g.* Kielich 1972, 1981) as well as their multipole polarizabilities (Amos 1979; Rivail and Cartier 1979; Espinoza *et al* 1979) are known.

The angular dependence of the correlation functions (115)–(118) assume a simple and at the same time elegant form if the Cartesian tensors are written in irreducible spherical tensor representation. With the spherical representation of the many-body distribution functions *e.g.* (107a, b) available, the calculations can be easily carried out to the end leading to results which are well adapted to numerical treatment. Nonetheless, the analytical expressions for the individual contributions are still mathematically bulky and we refrain from adducing them here.

10. Concluding remarks

Sections 7–9 contain but some of the more important applications of the general theory formulated in §5 comprising material hitherto not discussed in detail. The general expressions, of a high degree of complication from the mathematical viewpoint, reduce to a simpler form when one or another model is adopted. We then have to deal with rather straightforward problems, the concrete solutions of which are dependent on specific data available from the literature, thus (i) the mutually independent and non-zero tensor components of the intrinsic multipole moment and multipole polarizabilities for the various point groups in Cartesian representation (see *e.g.* Kielich 1972, 1981) or irreducible tensor representation (Gray and Lo 1976), and (ii) the possibility of calculating the radial binary, ternary averages $\langle r_{ij}^{-n} \rangle$, $\langle r_{ij}^{-n} r_{jk}^{-n} \rangle$, etc. for concrete models of the equilibrium correlation functions $g_{ij}^{(2)}$, $g_{ijk}^{(3)}$, ..., considered in the statistical theory of fluids (Ananth *et al* 1974; Blum and Narten 1976; Stell and Weis 1977; Larsen *et al* 1977; Wertheim 1980; Steinhauser and Neumann 1980; Haile and Gray 1980). Such concrete light scattering calculations have been carried out for atomic fluids and ones composed of spherical top molecules (Kielich 1960b, 1971b; Ralph and Gray 1974; Graben *et al* 1975; Alder *et al* 1979; Balucani *et al* 1979) as well as liquids with polar molecules (Woźniak and Kielich 1975, 1977).

The detailed treatment of these problems involves the finer fluctuational effects discussed on an advanced level in recently proposed molecular-statistical theories of the electric polarization of atomic and molecular fluids (see *e.g.* Titulaer and Deutch 1974; Høye and Stell 1980; Høye and Bedeaux 1977; Wertheim 1978, 1979; Felderhof 1979; Fulton 1979).

With regard to spectral studies, a considerable difficulty in the way of concrete applications of the formulae given in §§7–9 consists in the lack of analytical expressions for the time-space many body correlation function. Since Vineyard (1958) proposed his well known approximation of the binary correlation function, attempts have been

made recently aimed at determining the three- and four-body space-time correlation functions analytically (see *e.g.* Groome *et al* 1976; Gubbins *et al* 1978; Knast *et al* 1980). Our stochastic approach to scattered spectra taking into account changes in polarizability induced by space and time fluctuations of multipole fields involving, beside $G_{ij}^{(2)}(\mathbf{r}, t)$, the higher many-body correlation functions $G_{ijk}^{(3)}(\mathbf{r}, t)$, $G_{ijkl}^{(4)}(\mathbf{r}, t)$ enables us to gain simultaneously information regarding these functions inaccessible from other studies.

We have given considerable attention to the analysis of the cross contributions S_{01} , S_{02} , . . . , often neglected when analyzing experimental results. We have shown them to be of the same order of magnitude as S_{11} ; they are all the more interesting since they can be positive or negative, according to the electrical structure of the molecule and the model of ternary molecular correlations adopted. Obviously, we have by no means given all the possible contributions (*e.g.* the magneto-electric contributions, discussed in §4, are omitted) it being our sole aim to point out the potentialities inherent in the theory outlined above. The latter proves especially efficient in applications to two- and three-component systems, one component of which is composed of atoms and the others of spherical top (*e.g.* tetrahedral CCl_4 or octahedral SF_6), symmetric top (axially symmetric N_2 , CO_2 , C_6H_6 etc.), or asymmetric top molecules. In these cases, the spectral structure is described by new time-correlation functions. Clearly, the study of the Fourier transforms of these correlation functions is made easier by the use of the elegant formalism of irreducible spherical tensors (Chiu 1970; Özgo and Kielich 1976; Jerphagnon *et al* 1978; Tough and Stone 1979).

The by now well tested intermolecular (linear or two-photon) light scattering spectroscopy discussed above provides the foundations for the multiphoton scattering molecular spectroscopy developed more recently (Kielich 1981, 1983).

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On the coordination of molybdenum in AgI-Ag₂O-MoO₃ glasses using XANES and EXAFS

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Abstract. XANES and EXAFS analysis of the Mo *K*-edge spectra in a series of AgI-Ag₂O-MoO₃ glasses has been performed in order to determine the coordination of molybdenum in the glass. Mo has been found to exist in a tetrahedrally coordinated shell of four oxygens. Limitation of the EXAFS technique in discerning small distance differences in the first shell has also been discussed.

Keywords. EXAFS; XANES; coordination number; molybdate glass.

1. Introduction

Molybdenum trioxide, MoO₃, and silver molybdate, Ag₂MoO₄, along with silver iodide, AgI, have been used recently in the preparation of fast ion conducting glasses (Minami *et al* 1977; Hemlata *et al* 1983b). In the structural description of these glasses it is often implied that the oxymolybdate groups are present as MoO₄²⁻ tetrahedra or as corner shared Mo₂O₇²⁻ ditetrahedra. However, it is known that in MoO₃ and alkali polymolybdates molybdenum is present as MoO₆ octahedra (Anderson and Magneli 1950). Structures built with octahedra are more open and provide advantages particularly conducive to fast ion conduction. Since the spherical volumes swept by ionic (MoO₄) tetrahedra and (MoO₆) octahedra are identical, when MoO₆ octahedra are present a part of the oxygen ion volume may be looked upon as packed into the MoO₆ octahedra, thereby giving rise to a larger structural free volume. From a chemical point of view, maintaining an excess of oxygen-ion concentration in the system by incorporating a higher proportion of Ag₂O (than MoO₃) in the glass may be expected to favour such a situation. However, in earlier IR spectroscopic studies we obtained evidence only for the presence of tetrahedral MoO₄²⁻ ions, with the possibility that their symmetries could be lower than *T_d* (Hemlata *et al* 1983b). Therefore we felt it desirable to investigate the structure of oxygen polyhedra around the molybdenum ion in order to develop a structural model for this fast ion conducting glass system. Since it is known that a judicious combination of spectroscopic information from x-ray

Glasses in the system AgI-Ag₂O-MoO₃ were prepared by heating the required amounts of AgI, Ag₂O and MoO₃ (reagent grade) upto 800 K over a period of 3 hrs and quenching the resulting melts between polished glass plates. Glass formation was confirmed by observing the glass transition temperature in a differential scanning calorimetric run (Hemlata *et al* 1983b). The transparent glass discs so obtained were powdered to less than 400 mesh and mixed with puco cement. The slurry was cast into films by spreading it between microscope slides which were then slid apart to expose two identical films, and these were allowed to set in air. The concentration of the glass powder in slurry and the film thickness were manipulated so that the concentration of Mo across the thickness of the resulting film was equivalent to 1–2 absorption lengths at the K-absorption edge of Mo (19·999·5 eV).

The XANES and EXAFS spectra were recorded with the C-2 spectrometer at CHSS (Cornell High Energy Synchrotron Source) with CESR (Cornell Electron Storage Ring) running at 5·3 GeV and an injection current of 12–15 mA. Three glasses with compositions of 60 AgI·20 Ag₂O·20 MoO₃, 40 AgI·30 Ag₂O·30 MoO₃ and 55 AgI·25 Ag₂O·20 MoO₃ were investigated. Na₂MoO₄ and MoO₃ were initially chosen as model compounds to compare the near edge features and to obtain phase parameters. MoO₄²⁻ ions in Na₂MoO₄ are known to be tetrahedral (Lindquist 1950; Clark and Doyle 1960) with Mo-O distance of 1·83 Å. The octahedron of oxygens in MoO₃ is distorted and there are five Mo-O distances (Anderson and Magneli 1950) which make it less suitable as a model compound.

Spectra were recorded repeatedly (5–6 times) with a large I₀ count of 50,000–100,000 and spectral features were confirmed to be free from artefacts resulting from any spurious effects arising from either radiation source or experimental sample. Pre-edge and post-edge back-ground removal, edge normalization, extraction of the EXAFS signal $\chi(k)$, Fourier transformation of $\chi(k)$, and inverse Fourier transformation of the first peak in the radial structure function (in order to isolate $\chi(k)$ from the first shell) were performed using procedures described elsewhere (Lytle *et al* 1975; Lee *et al* 1981; Wong 1981). On obtaining the normalised XANES spectra the pre-edge region (–220 to –50 eV) was linearly fitted and extrapolated above the edge. The post-edge back-ground in the EXAFS region was generated analytically using a series of cubic splines of equal length (DeBoor 1968). The ends of each segment were so connected as to make their derivatives continuous across the ends and five such segments were found adequate.

The energy scale was converted to the k scale using the relation $k = (1/\hbar) [2m(E - E_b)]^{1/2} = 0·263 (E - E_b)^{1/2}$, where E_b is the Mo-K-edge energy. The normalised EXAFS, $\chi(k)$ at energies above 30 eV was obtained using the relation $\chi(k) = [\mu(k) - \mu_0(k)]/S \cdot M(k)$, where $\mu(k)$ is the measured absorption, $\mu_0(k)$ is the smooth post-edge background, S is the step jump at the absorption edge and $M(k)$ the McMaster (1969) correction energy function.

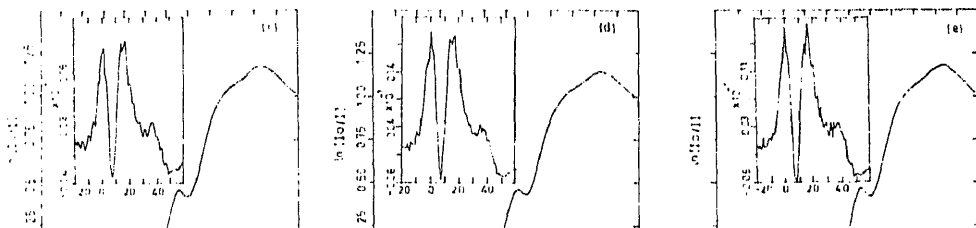
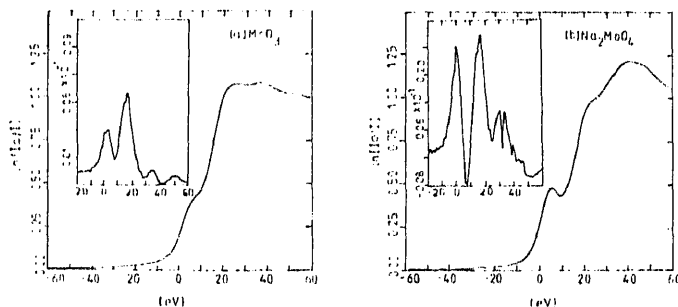
3. Results and discussion

The near edge spectra at the Mo-K-edge (XANES) of MoO₃ (a) Na₂MoO₄ (b) and the three glasses, (c) (60 AgI·20 Ag₂O·20 MoO₃), (d) (40 AgI·30 Ag₂O·30 MoO₃) and

(e) ($55 \text{ AgI} \cdot 25 \text{ Ag}_2\text{O} \cdot 20 \text{ MoO}_3$), are shown in figure 1. The differentiated spectra are given as insets. Results of the Mo-K-edge EXAFS analysis of Na_2MoO_4 and the three glasses c, d and e are given in figures 2, 3, 4 and 5 respectively. In Na_2MoO_4 only discrete tetrahedral MoO_4^{2-} ions are known to be present, while in MoO_3 molybdenum is known to be present in distorted octahedra. (Lindquist 1950; Clark and Doyle 1960). In view of the similarity of the near edge spectra of the glasses to that of Na_2MoO_4 rather than to that of MoO_3 , Na_2MoO_4 was chosen as the model compound. Since Mo^{6+} is coordinated by four oxygen ions at identical distances, the EXAFS from Na_2MoO_4 was self-fitted to obtain both amplitude and phase parameters. The phases were fitted into a four parameter (Lee *et al* 1977) equation:

$$\phi = P_0 + P_1 k + P_2 k^2 + P_3 / k^3 \quad (1)$$

and the best fit values were $P_0 = 5.8216$; $P_1 = 1.4941$; $P_2 = 0.0403$ and $P_3 = 77.25$. Using the phase and amplitude parameters from the EXAFS of the Mo-K edge in Na_2MoO_4 , the Mo-EXAFS of the three glasses were examined. The procedure for analysis of the EXAFS data has been given in detail elsewhere (Teo and Lee 1979; Rao *et al* 1983). Briefly an assumed value of the number of neighbours (N_j) and their distances (R_j) were given as input parameters along with guesstimate values of σ_j , the spread in the first neighbour distances (a parameter analogous to the Debye-Waller term in x-ray diffraction analysis). The EXAFS of the first shell ($j = 1$) was obtained by the inverse Fourier transform of the first peak in the radial structure function (between 0.5 Å to 1.85 Å for all glasses). Fitting to the theoretical EXAFS was performed using the



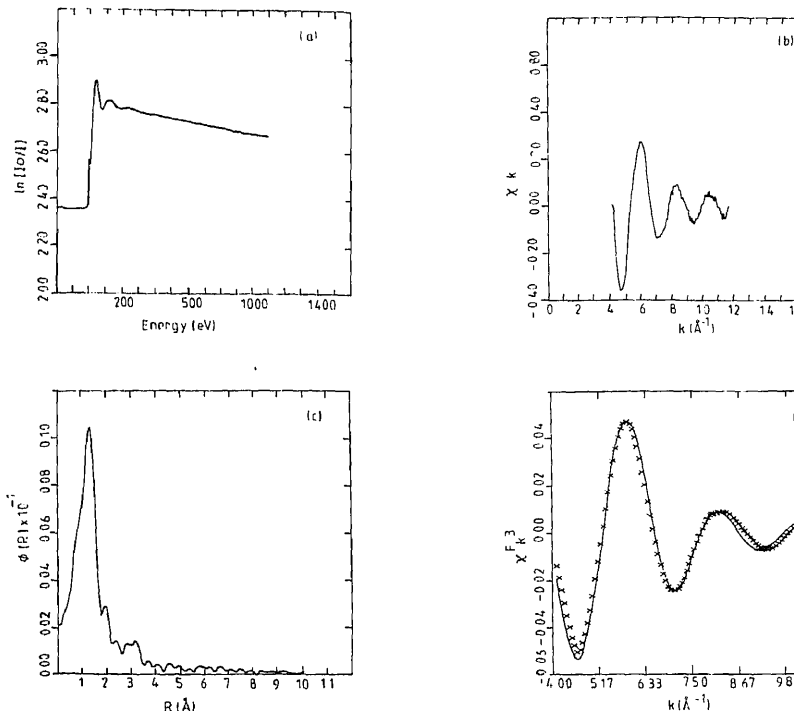


Figure 2. Various stages of EXAFS analysis of the model compound Na_2MoO_4 . (a) Mo-K-edge spectrum, (b) normalized EXAFS trace, (c) radial structure function obtained Fourier transform of (b), (d) inverse Fourier transform (solid line) and simulated (crosses) of the first peak from (c) (see text for other details).

expression:

$$\chi(k) = \frac{-1}{k} \sum A_j \sin [2R_j k + \phi_j(k)]$$

with $j = 1$. Where A_j is given by:

$$A_j = (N_j/R_j^2) f_j(\pi, k) \exp(-2R_j/\lambda) \exp(-2\sigma_j^2 k^2).$$

The results of the theoretical fit for the three glasses are shown in figures 3(d), 5(d). Self-consistent N_j , R_j and σ_j values thus obtained are given in table 1 along the standard deviation (percentile fitting to the experimental EXAFS). The M distances obtained from EXAFS analysis appear to be in excellent agreement with values reported in literature (Clark and Doyle 1960) and are also consistent in the glasses. The number of neighbours appears to be close to four within about 10-1. Therefore the analysis supports that the molybdate ions are present as MoO_4 tetrahedra in these glasses.

3.1 Near edge spectra

The tetrahedrality of oxygen coordination is also supported by the near edge spectra shown in figure 1. The spectra of Na_2MoO_4 and the three glasses are very similar.

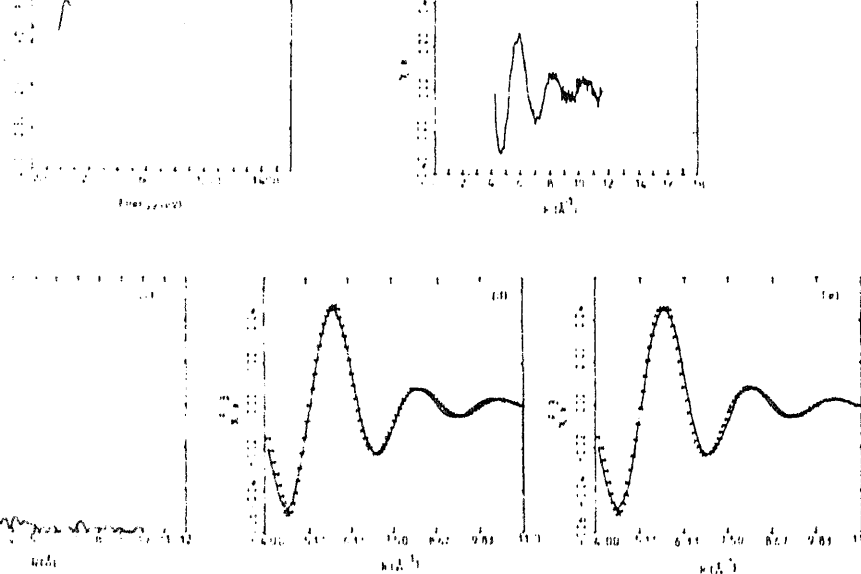


Figure 3. EXAFS analysis of 60 AgI · 20 Ag₂O · 20 MoO₃ glass, (a), (b) and (c) have the same significance as in figure 2. (d) and (e) are inverse Fourier transform and theoretical fit using one and two oxygen shells respectively.

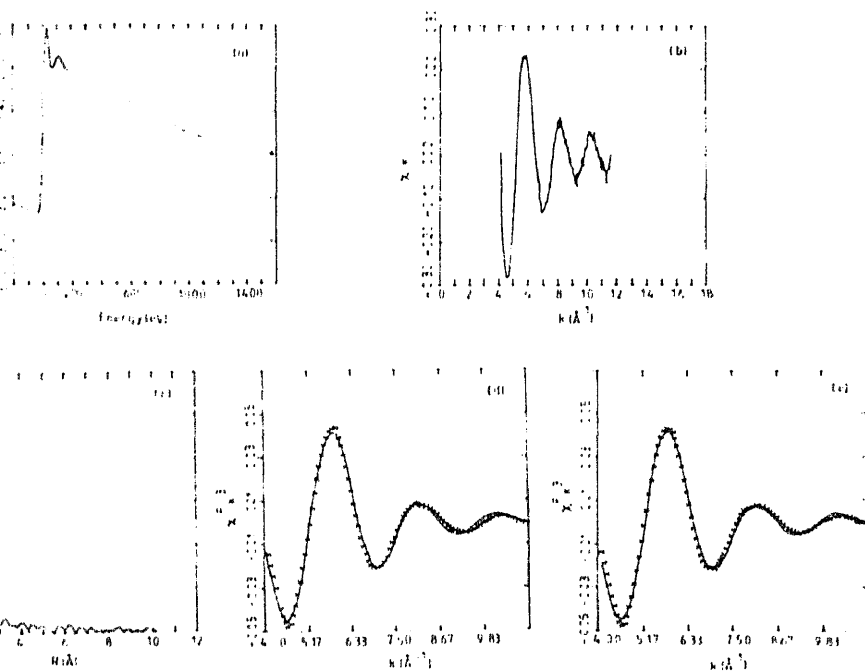


Figure 4. EXAFS analysis of 40 AgI · 30 Ag₂O · 30 MoO₃ glass (a), (b), (c), (d) and (e) have the same significance as in figure 3.

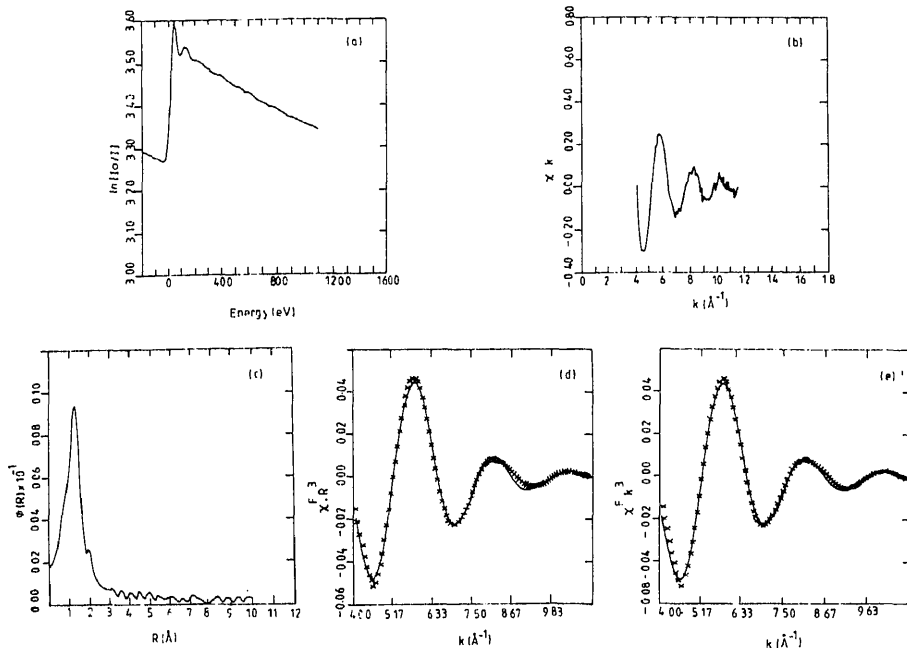


Figure 5. EXAFS analysis of 55 AgI·25 Ag₂O·20 MoO₃ glass. (a), (b), (c), (d) and (e) have the same significance as in figure 3.

Table 1. Coordination number and structural parameters from EXAFS analysis of AgI·Ag₂O·MoO₃ glasses.

Glass composition AgI:Ag ₂ O:MoO ₃	Coordination number <i>N</i>	<i>R</i> (Å)	σ^2 (Å) ² × 10 ²	Standard deviation %
1. One shell				
60:20:20	4.54	1.839	0.216	3.7
40:30:30	4.22	1.837	0.199	3.7
55:25:20	4.57	1.838	0.237	3.7
2. Two shells				
60:20:20	3.20	1.830	0.159	3.9
	1.19	1.923	0.031	
	3.13	1.831	0.156	
40:30:30	1.06	1.923	0.121	3.9
	3.27	1.829	0.164	
55:25:20				4.1

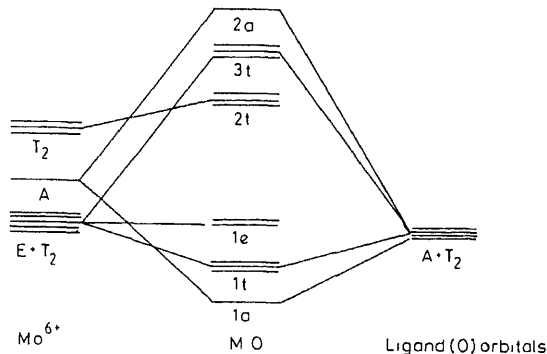


Figure 6. Schematic molecular orbital diagram for MoO_4^{2-} ions.

While there is remarkable overall similarity in the differentiated spectra (insets to figure 1) of Na_2MoO_4 and the glasses, there are certain clearly recognisable differences; the second peak of the differentiated spectra appears to be split in the case of the glasses. If the molybdate ions were all ideally tetrahedral, the transition should be consistent with the schematic molecular orbital diagram for MoO_4^{2-} ion shown in figure 6. The diagram has been drawn using only those orbitals of the ligands which form σ bonds with the central Mo atom. The first two peaks, one low intensity peak and the immediately next intense peak in the spectra of Na_2MoO_4 and the glasses arise from transitions of the molybdenum $1s$ (not shown) electrons to $1e$ and $1t$ m.o. levels. The forbiddenness of the transition to $1e$ level is slightly relaxed in T_d symmetry (Grunes 1982). Still higher energy transitions (> 30 eV) can originate either from shape-resonances (Rao and Wong 1984) or from any shake-up processes (Rehr *et al* 1978).

Since the 2nd peak in the differentiated spectra of the glasses appears to be split, one could speculate on the possibility that the symmetry of the oxygen coordination shell around Mo is lower than T_d . Since these glasses are coloured and their electronic conductivity is not negligible (Minami *et al* 1980), there is a possibility that at least a small fraction of the molybdate ions contain molybdenum in the Mo^{5+} state. Evidence for the presence of Mo^{5+} has been obtained from electron spin resonance studies (unpublished results from this laboratory) and the Mo^{5+} ion may be expected to suffer Jahn-Teller distortion. Further, from the point of view of the cluster model (Rao and Rao 1982; Parthasarathy *et al* 1983; Rao 1984) which has been very successfully applied to the present system of glasses (Hemlata *et al* 1983a; Hemlata *et al* 1984), a substantial portion of the MoO_4^{2-} ions are expected to be present in the truly disordered tissue region of the glass. These MoO_4^{2-} ions (of the tissue region) could be somewhat distorted. Hence, either due to the Jahn-Teller effect in Mo^{5+} ions or due to structural reasons, a substantial portion of the tetrahedra are likely to be distorted causing a split in $1t$ levels. This could be the origin of the splitting observed in the differentiated spectra. Hence more than one Mo-O distance is likely to be present in MoO_4^{2-} ions.

In order to investigate the possible distortion of MoO_4^{2-} ions which gives rise to different Mo-O distances the EXAFS on these glasses were re-analysed assuming that there are two oxygen each at two different distances ($j = 2$ in (2) where j now represents a number of sub-shells). Corresponding EXAFS fits are shown in figures 3(e), 4(e) and 5(e)

table 1. It is found that the standard deviation has not worsened by the revised fitting and a two-shell fitting appears quite feasible because the coordination number from the fit turns out to be closer to four than in the case of single-shell fitting. The disorder parameter, σ also improves in the sense that it decreases to magnitudes which are in the range of the limit of distance resolution in EXAFS experiments (± 0.02 Å).

However, such improved fitting raises a fundamental question, namely whether EXAFS procedures generally adopted are capable of discerning such small differences in bond distances in the first-shell of neighbours so as to enable one to comment on the geometry of the first coordination polyhedra. In view of the multiparametric nature of phase-analysis of the model compound and of the fitting procedures employed, it is possible that the EXAFS technique at its present stage of development may also give rise to inherent errors in situations of the present kind.

Acknowledgements

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Viscosities of binary liquid mixtures of polar-apolar and polar-polar systems at 303.15 K

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Abstract. Viscosities for the binary liquid mixtures of methylethylketone with benzene, toluene, chlorobenzene, bromobenzene and nitrobenzene were determined at 303.15 K. The deviation in viscosity was calculated and its behaviour was studied as a function of mole fraction. The deviation in viscosity is negative in the system methylethylketone with benzene and is positive in the other systems. The results are discussed in terms of dipole-induced dipole and dipole-dipole interactions.

Keywords. Excess viscosity; molecular interactions; polarizability.

1. Introduction

As part of a study of viscosities of liquid mixtures (Reddy and Naidu 1979, 1981) we have measured the viscosities for methylethylketone with benzene, toluene, chlorobenzene, bromobenzene and nitrobenzene to investigate the molecular interactions. These systems have been selected for studying the effect of molecular interactions due to substitution of different groups on benzene ring, along with benzene in presence of a polar component. A literature survey has shown that the viscosity data for these systems have not been reported except for methylethylketone with benzene system at 308.15 K (Yadava and Yadava 1981).

2. Experimental

Viscosities of pure liquids and mixtures were measured at 303.15 K using an Ostwald viscometer and were accurate to 0.5 per cent. Densities for the pure components were measured using a bicapillary pycnometer and in case of mixtures densities were obtained from excess volume, V^E , data (Jayalakshmi and Reddy 1983) using the relation

$$\rho = \frac{x_1 M_1 + x_2 M_2}{x_1 V_1 + x_2 V_2 + V^E} \quad (1)$$

Density values in both the cases were accurate to $\pm 5 \times 10^{-5} \text{ g cm}^{-3}$.

Methylethylketone, benzene and toluene (all BDH) were purified by methods described earlier (Reddy and Naidu 1977, 1978). Chlorobenzene (BDH), bromobenzene

(E Merck) and nitrobenzene (BDH) were dried over calcium chloride and fractionally distilled. The purity of the samples was ascertained by comparing the values of density, boiling point and refractive index with the literature values (Timmermans 1950, 1965).

3. Results and discussion

The values of density and viscosity are given in table 1. Excess viscosities are calculated using the relation

$$\Delta \ln \eta = \ln \eta - (x_1 \ln \eta_1 - x_2 \ln \eta_2). \quad (2)$$

The values of $\Delta \ln \eta$ are accurate to ± 0.005 and are included in table 1. Excess viscosities are represented by an empirical equation of the form

$$\Delta \ln \eta = x_1 x_2 [A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2]. \quad (3)$$

The values of the constants A_0 , A_1 and A_2 are obtained by the method of least squares and are given in table 2 along with the standard deviation $\sigma(\Delta \ln \eta)$.

The data included in table 1 show that the excess viscosity is negative in the system methylethylketone with benzene and the values are positive in the remaining systems. The observed data may be explained on the basis of the following factors, mutual loss of dipolar association due to addition of second component and difference in polarizabilities, size and shape of the components (Yadava and Yadava 1981). In the system methylethylketone with benzene, the dipolar association of ketone breaks when benzene is added, further a weak dipole-induced dipole interaction may arise between unlike components. As a result the mixture becomes more fluid (less viscous) than the pure components and the deviation in excess viscosity becomes negative. The positive deviation in excess viscosity observed in the system methylethylketone with toluene may be ascribed to the presence of a methyl group in toluene which increases the π -electron density in the aromatic ring due to the hyperconjugation effect. Consequently, molecular interactions may be enhanced in mixtures and become less fluid than the pure components. In the systems methylethylketone with chlorobenzene, bromobenzene and nitrobenzene a strong dipole-dipole interaction may be present between unlike molecules. Thus the flow may be further decreased and excess viscosity becomes more positive. The algebraic values of $\Delta \ln \eta$ fall in the order shown for the five systems:

$$\text{benzene} < \text{toluene} < \text{nitrobenzene} < \text{chlorobenzene} < \text{bromobenzene}.$$

This order is not in parallel with the order in polarizabilities of the noncommon components. On the basis of polarizabilities $\Delta \ln \eta$ values are expected to be more positive in the system methylethylketone with nitrobenzene than in the systems methylethylketone with chlorobenzene and bromobenzene. This discrepancy in the order may be attributed to the difference in size and shape of the substituted groups.

The values of the coefficients A_0 , A_1 and A_2 given in table 2, indicate the nature of molecular interactions with respect to mole fraction (Prausnitz 1969). The values of A_0 and A_2 may contribute to the understanding of the extent of symmetric interactions whereas the values of A_1 suggest the extent of unsymmetric interactions. The percentage contribution of A_1 increases from benzene to nitrobenzene. This shows that

Table 1. Mole fraction of methylethylketone x_1 , densities ρ , viscosities η , and excess viscosities at 303.15 K.

x_1	$\frac{\rho}{\text{g cm}^{-3}}$	$\frac{\eta}{\text{CP}}$	$\ln \eta$	$\Delta \ln \eta$
<i>Methylethylketone + benzene</i>				
0.0000	0.86841	0.573	-0.557	—
0.1023	0.86122	0.538	-0.620	-0.021
0.2042	0.85405	0.509	-0.675	-0.033
0.3950	0.84045	0.467	-0.762	-0.041
0.5129	0.83179	0.444	-0.811	-0.037
0.6822	0.81905	0.420	-0.868	-0.027
0.8530	0.80587	0.396	-0.926	-0.014
1.0000	0.79443	0.378	-0.973	—
<i>Methylethylketone + toluene</i>				
0.0000	0.85922	0.531	-0.634	—
0.1009	0.85426	0.516	-0.661	0.006
0.2412	0.84681	0.496	-0.701	0.014
0.3948	0.83807	0.475	-0.744	0.023
0.5240	0.83010	0.458	-0.781	0.030
0.7006	0.81815	0.431	-0.842	0.029
0.8899	0.80368	0.397	-0.942	0.012
1.0000	0.79443	0.378	-0.973	—
<i>Methylethylketone + chlorobenzene</i>				
0.0000	1.09660	0.721	-0.327	—
0.0982	1.07118	0.686	-0.377	0.013
0.2470	1.03102	0.636	-0.452	0.034
0.3771	0.99433	0.593	-0.523	0.047
0.5481	0.94370	0.541	-0.614	0.067
0.6776	0.90350	0.499	-0.695	0.069
0.8508	0.84673	0.482	-0.730	0.046
1.0000	0.79443	0.378	-0.973	—
<i>Methylethylketone + bromobenzene</i>				
0.0000	1.48440	1.007	0.007	—
0.1487	1.39665	0.899	-0.106	0.032
0.2073	1.36081	0.858	-0.153	0.042
0.3888	1.24529	0.740	-0.301	0.072
0.5263	1.15241	0.656	-0.422	0.086
0.7046	1.02473	0.556	-0.587	0.096
0.8307	0.92914	0.486	-0.720	0.087
1.0000	0.79443	0.378	-0.973	—
<i>Methylethylketone + nitrobenzene</i>				
0.0000	1.19330	1.613	0.478	—
0.1487	1.14328	1.320	0.278	0.016
0.3244	1.08003	1.039	0.039	0.032
0.4126	1.04681	0.925	-0.078	0.043
0.4992	1.01309	0.820	-0.198	0.048
0.7145	0.92461	0.607	-0.501	0.059

Table 2. The constants of (3) and the standard deviation.

Methylethylketone +	A_0	A_1	A_2	$\sigma(\Delta \ln \eta)$
Benzene	-0.151	0.076	-0.027	0.001
Toluene	0.115	0.043	-0.033	0.002
Chlorobenzene	0.250	0.151	0.024	0.002
Bromobenzene	0.335	0.265	0.222	0.003
Nitrobenzene	0.197	0.172	0.102	0.001

+ Signifies the representation of mixture, for example, methyl-ethylketone benzene, etc.

polar-apolar systems. This behaviour is also evident from excess viscosity versus mole fraction data in which the maximum values of $\Delta \ln \eta$ are shifting towards higher mole fractions of ketone in the series from benzene to nitrobenzene.

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Viscometric studies of hydrogen bonding

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Abstract. The viscometric method can be conveniently used for studying the interaction between weakly interacting systems. The systems studied are: methanol-acetone, ethanol-acetone, *n*-propanol-acetone and *n*-butanol-acetone in carbon tetrachloride. At 25°C, the equilibrium constants for the above ternary systems are 0.22, 0.30, 0.38 and 0.52 M⁻¹ respectively. However, the heats of formation of complexes obtained by the viscometric method are high and decrease from methanol-acetone-CCl₄ to *n*-butanol-acetone-CCl₄.

Keywords. Hydrogen bonding; viscometry; equilibrium constants.

1. Introduction

Although the spectrophotometric method is probably the most common method used for determining association constants and other thermodynamic parameters of charge-transfer complexes, doubts have frequently been expressed as to the significance of the values, K_c , and ϵ , obtained by the spectral method alone (Childs *et al* 1971, 1972). It is surprising that even though, in principle, the formation of molecular complexes and hydrogen bonding can be detected and their composition established from a study of characteristic abrupt departures from ideal behaviour in some physical properties, *e.g.* vapour pressure, refractive index, surface tension and viscosity etc., many of these methods are hardly used (Vinogradov and Linnel 1971). Recently we have begun the exploration of some non-spectral methods for studying the interaction between the molecules in solution and have demonstrated their applicabilities in obtaining the equilibrium constants directly (Singh and Bhat 1978; Singh *et al* 1980; Bhattacharjee and Bhat 1983). Even though the measurements of various thermodynamic excess functions of binary solutions (using viscometry) have been the subject of much research, there is hardly any report on using viscosity measurement method for ternary systems (Irving and Smith 1969). It was therefore felt that it was worthwhile to make an attempt to study the interaction between proton donors and proton acceptors (*i.e.*, hydrogen bonding) viscometrically, in suitable media and to obtain equilibrium constants directly. The systems chosen for the studies are: methanol, ethanol, *n*-propanol and *n*-butanol as proton donors, acetone as proton acceptor, and carbon tetrachloride as solvent.

2. Materials and method

Acetone, carbon tetrachloride, methanol, ethanol, *n*-propanol and *n*-butanol were purified by standard procedures. The densities and the corrected boiling points agreed well with literature data.

The densities and viscosities of pure samples and those of 'binary mixtures' of known composition (mole fractions) of methanol, ethanol, *n*-propanol, *n*-butanol and acetone in carbon tetrachloride were determined at 25, 30, 35 and 40°C ($\pm 0.1^\circ\text{C}$) by using a pycnometer and Ostwald's viscometer respectively and coefficients of viscosity were calculated. Similarly the densities and viscosities of ternary systems (of known composition) of alcohols-acetone- CCl_4 were determined. The experiments were repeated at least twice and the results were reproducible within the experimental error of $\pm 0.015 \times 10^{-3}$ poise.

The stoichiometry of the 'associated species (complex)' was determined by Job's continuous variation process (Job 1928).

The non-linear plot of any physical property of a 'mixed solution' against the concentration of the components, i.e. the deviation from ideal behaviour of the pure components in solution is an indication of the interaction between the two species, namely the donor D, and the acceptor A (after deducting the solvent contributions). If one can assume that the deviation is entirely due to the 'complex' alone, then the deviation should be proportional to the concentration of the complex. We have modified the procedure suggested by Yoshida and Osawa (1965) to obtain the equilibrium constant, K_c . The detailed procedure is given in Bhattacharjee and Bhat (1983).

3. Results and discussion

The viscosities of methanol, ethanol, *n*-propanol, *n*-butanol, acetone and carbon tetrachloride were determined at 25, 30, 35 and 40°C. The viscosity of methanol in carbon tetrachloride is higher than the expected value [i.e., $\Delta\eta = \eta_{\text{obs}} - \eta_{\text{cal}} = -\eta_{\text{obs}} - (x_1\eta_1 + x_2\eta_2)$] whereas in all other alcohols they are lower. The deviation in η value (i.e., $\Delta\eta$) shows that there is interaction between methanol and carbon tetrachloride and the maximum deviation is at 3:2 composition, which is temperature independent. As the observed values are higher than the expected values, it appears that due to 'complexation'/'association' between CH_3OH and CCl_4 molecules the viscosity has increased. Similar is the case for acetone- CCl_4 systems (2:3). It is known that acetone and carbon tetrachloride do interact to form a complex (Rao *et al* 1972; Rowlinson 1971). Singh and Rao (1967) studied the infrared spectra of methanol and showed that alcohols formed dimers or trimers in carbon tetrachloride solutions as dilute as 0.01 M. An NMR study by Dixon (1970) of methanol in CCl_4 showed the existence of trimers and octamers even in very dilute solutions. Therefore it is quite safe to assume that methanol etc. associate through hydrogen bonding in carbon tetrachloride solutions. So when carbon tetrachloride approaches alcohol molecules, there is a 'breaking' of the hydrogen bonding in associated alcohol molecules and formation of H-bonds with CCl_4 (Patterson and Hammaker 1967). Methanol is a small molecule (as compared to other alcohol molecules), the dimerization energy in methanol is maximum and it decreases from methanol to *n*-butanol (Vinogradov 1971). As the dimerization energy is greater for methanol molecules, stability of associated species is higher. Hence

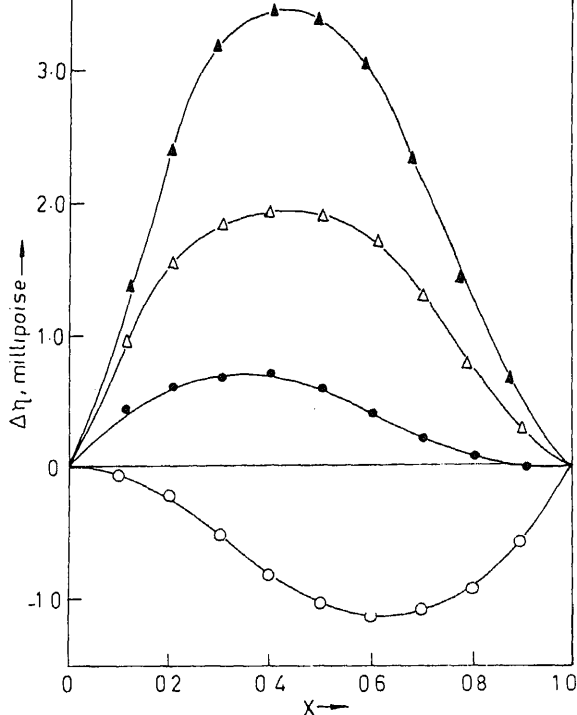


Figure 1. Variation of $\Delta\eta$, the difference between the η_{obs} and η_{cal} with the mole fraction of alcohols; (1) MeOH-carbon tetrachloride ($\circ$ — $\circ$ — $\circ$); (2) EtOH-carbon tetrachloride ($\bullet$ — $\bullet$ — $\bullet$); (3) *n*-PrOH-carbon tetrachloride ($\triangle$ — $\triangle$ — $\triangle$); (4) *n*-BuOH-carbon tetrachloride ($\blacktriangle$ — $\blacktriangle$ — $\blacktriangle$).

MeOH-CCl₄ < EtOH-CCl₄ < *n*-PrOH-CCl₄ < *n*-BuOH-CCl₄, indicating that MeOH-CCl₄ interaction is less favoured as compared to *n*-BuOH-CCl₄ (figure 1). The stoichiometry is 2:3 in EtOH-CCl₄, *n*-PrOH-CCl₄ and *n*-BuOH-CCl₄. Similar observations are reported in literature for higher alcohols-dichloromethane mixtures (Choudhury and Naidu 1981; Reddy and Naidu 1977). The deviation decreases with increase in temperature. The energy of activation (for viscous flow) of pure components, namely, methanol, ethanol, *n*-propanol, *n*-butanol, acetone and carbon tetrachloride are 10.5, 16.9, 19.1, 21.0, 6.9 and 10.9 kJ mole⁻¹ respectively and the corresponding values of the alcohols and acetone in CCl₄ are 10.5, 11.9, 12.7, 13.4 and 7.6 ± 0.01 kJ mol⁻¹ respectively. From these data it is clear that activation energy increases with the size of the molecules. Even though one would like to conclude that the viscosity and the energy of activation depend on the size of the molecule, one has to be cautious in cases like the present one, involving already 'associated' species and probably more than one H-bonded species between donor and acceptor molecules. It can be seen from the above data that the energies of activation of the 'mixtures' of alcohol-CCl₄ are lower than that of alcohol itself, which we are not in a position to explain, however, as we are dealing with 'complex'/'associated' molecules.

The viscosities of ternary systems, namely alcohol-acetone-carbon tetrachloride of

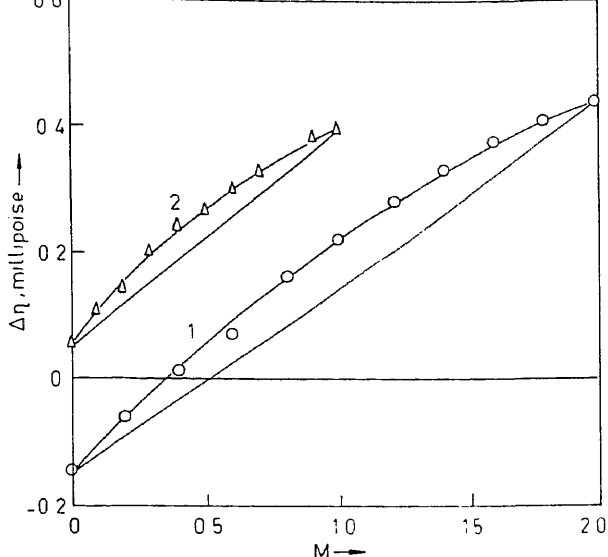


Figure 2. Variation of $\Delta\eta$, with molar concentration of acetone in MeOH-acetone-carbon tetrachloride, system at 25°C; (1) total concentration = 2 mole (○); (2) total concentration = 1 mole (Δ).

No maxima are found in the viscosity curves. But the non-linear plot of the difference in viscosities of the mixed solutions (i.e., $\eta_{\text{cal}} - \eta_{\text{obs}}$) against the concentration of acetone indicates the presence of a complex. A continuous variation plot of $\Delta\eta$, the difference in viscosity between the 'mixed solutions' and the calculated viscosities of the two solutions, shows the presence of a 1:1 complex in the experimental range of concentration (figure 2). From the figure it is clear that there is interaction between acetone and alcohol in CCl_4 . The interaction (area under the curve in the plot) increases from MeOH-acetone- CCl_4 to *n*-BuOH-acetone- CCl_4 systems; this indicates the relative strength of the 'complexes', i.e., *n*-BuOH-acetone- CCl_4 > *n*-PrOH-acetone- CCl_4 > EtOH-acetone- CCl_4 > MeOH-acetone- CCl_4 . The equilibrium constants were calculated (from the concentrations of the species rather than the activities) and at 25°C they are 0.22, 0.30, 0.38 and 0.52 M^{-1} for MeOH-acetone, EtOH-acetone, *n*-PrOH-acetone and *n*-BuOH-acetone in CCl_4 respectively. Here it is worth mentioning that Tamres and Strong (1979) have rightly pointed out that even contact charge-transfer complexes should have *K* values of the order of 0.11 M^{-1} . From the above data it is clear that the formation constant for the hydrogen bonded complex increases from MeOH-acetone to *n*-BuOH-acetone, assuming that the standard enthalpy of formation ΔH° of the hydrogen bond in a complex $\text{A-H} \cdots \text{B}$ and its standard entropy of formation ΔS° are independent of temperature. The heat of formation of these complexes were obtained from the plot of $\log K_c$ vs $1/T$ and these values are slightly higher than normal ($-\Delta H^\circ$ for MeOH-acetone, EtOH-acetone, *n*-PrOH-acetone and *n*-BuOH-acetone in CCl_4 are 63.4, 46.5, 40.7, 37.5 kJ/mole respectively). However, similar observations were made in literature for purine- H_2O -DMSO (Kanbour *et al* 1983) heterocyclic compounds-phenol (Sverdlov and Vatulina 1983) malamine

Table 1. Equilibrium constants and other thermodynamic parameters of *n*-alcohols-acetone in carbon tetrachloride.

System	$K_c^* \text{ M}^{-1} \dagger$				$-\Delta H^{0**}$	$-\Delta G^0$	$-\Delta S^0$
	25°C	30°C	35°C	40°C	kJ/mole	kJ/mole at 25°C	kJ/mole
MeOH-acetone	0.22	0.16	0.09	0.07	63.5	-3.1	0.22
EtOH-acetone	0.30	0.22	0.17	0.12	46.5	-2.9	0.17
<i>n</i> -PrOH-acetone	0.38	0.25	0.21	0.17	40.7	-2.7	0.15
<i>n</i> -BuOH-acetone	0.52	0.41	0.31	0.27	37.5	-1.6	0.13

* K_c values were calculated from the K_x values, by using the equation, $K_x = \frac{K_c 1000 d_s}{M_s}$ where, d_s = density of

the solvent in g/ml, M_s = Molecular weight of the solvent.

† Error limit = ± 0.01 ; ** error limit = ± 1.5 .

cyanourate (Finkelshtein and Rukerich 1983). It may be recalled that the large enthalpies (≈ 60 kJ/mole) of formation of the complexes of nitrophenols with picric acid have been explained in terms of 1:1 proton transfer complexes in preference to the 1:1 H-bonded complexes (Vinogradov 1971). However, in the present case we are not able to account for such high values of ΔH . Kohler (1984) has pointed out that it is difficult to compare the nonspectroscopic and spectroscopic evaluation of complexation equilibria (and other thermodynamic parameters) because nonspectroscopic—thermodynamic properties are determined by the activities of the species whereas spectroscopic properties are determined by their concentration. The values for the heats of complexation must be considered as presenting a composite result for alcohol-acetone- CCl_4 systems of different alcohol aggregation (Tse and Tamres 1977). The process of self association and preferential solvation results in a complex which seems to consist of acetone molecule interacting with an aggregate containing many alcohol molecules. The number of alcohol molecules in the aggregate is concentration dependent because of different degrees of self association and solvation. It is possible that the donor strength of the alcohol may change after association. Molecular orbital calculations on the association of water, of methanol and of other hydrogen bonded molecules show that the charge distribution of the polymeric molecule is different from that of the monomer (Hoyland and Kier 1969; Murthy *et al* 1969, 1970; Marita and Nagakura 1972). The negative charge on the oxygen atom in the molecule acting as the proton donor increases when the hydrogen bond is formed, and increases further if a trimer is formed, this in turn causes greater positive charge on the proton and the interaction between the proton and the oxygen of acetone is stronger. For an exothermic reaction, ΔG^0 is negative. However, in the present case ΔG^0 is positive ($K < 1$); and ΔS^0 is negative and this is possible because of the large negative ΔH^0 .

As mentioned in our earlier communication, even though the usefulness of the viscometric method in the study of molecular complexes has already been established, the present procedure demands very careful measurements of viscosities involving long flow times in order to realise significant difference between solvent and dilute solutions.

from dust, grease, etc. Moreover, the measurements are intrinsically time consuming. So even though the viscometric method can be used for studying the interaction between molecules in solution it may be more applicable where no alternative is available.

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Alkaline hydrolysis of arylestere of diphenylphosphorodiamidates—evidence consistent with an elimination—addition mechanism

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Abstract. The alkaline hydrolysis of a series of aryl phosphorodiamidates has been studied in aqueous ethanol and aqueous DMSO mixtures. Although the reactions do not show any saturation kinetics with respect to the hydroxide ion, the low solvent isotope effect, the highly negative Bronsted β value, the large Hammett ρ for the leaving aryloxy group and the decrease in rate with increase in the proportion of DMSO in the solvent mixtures indicate that the hydrolysis proceeds by an elimination–addition pathway. Comparison of rate data with other hydrolytic E1CB reactions show that the title reaction belongs to the (E1CB)_R category.

Keywords. Diphenylphosphorodiamidate esters; alkaline hydrolysis; E1CB mechanism.

1. Introduction

Esters and halides of phosphorodiamidates have two modes of decomposition for alkaline hydrolysis an SN2(P) mechanism and an E1CB mechanism. Evidence for the latter mechanism has accumulated in recent times on the basis of the large difference in the values of the alkaline hydrolysis rate constant of mono- and disubstituted nitrogen esters and halides. The rate enhancement was higher than could be ascribed to the steric hindrance to the approach of the OH[−] in an SN2(P) mechanism (Gerrard and Hamer 1967). Structure-reactivity correlations used extensively to establish the operation of this mechanism in the hydrolysis of carbamate (Williams 1972) and arylmethane sulphonates (Williams and Douglas 1974) have been applied to study this hydrolysis and decide in favour of the E1CB mechanism (Williams and Douglas 1972). We have shown earlier that a discriminating effect of a dipolar aprotic solvent such as DMSO can be used to differentiate between an SN2 and an E1CB mechanism in the case of carboxylic esters and arylphenylmethane sulphonates (Krishnan *et al* 1978, 1979 and 1982). We report in this communication an extension of this theory as also a structure-reactivity analysis to the case of phosphorodiamidates to decide the mechanism of alkaline hydrolysis of this system.

2. Experimental

Substituted phenyl N,N-diphenylphosphorodiamidates were prepared according to the method of William and Douglas (1972). The melting points obtained (table 1) agree

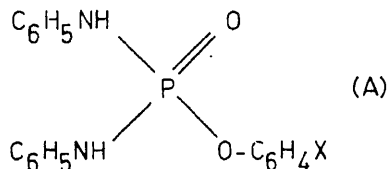
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with literature values. Dimethyl sulphoxide (DMSO) was purified under reduced pressure in an all-glass apparatus over calcium hydride (b. pt. 95–96°C; 31 mm) and stored in air-tight bottles. The rates of alkaline hydrolysis of the various esters used were followed using a Carl-Zeiss VSU2-P model spectrophotometer by following the release of the phenoxide ion at appropriate wavelengths. Pseudo first-order rate constants for the hydrolysis were calculated from the slopes of the plots of $\log (A_{\infty} - A_t)$ versus time. The method of least squares was employed and the slopes and correlation coefficients were determined by using a Micro 2200 programmable calculator (Hindustan Computers). The alkaline hydrolysis of *p*-nitrophenyl N,N'-diphenylphosphorodiamidates was also followed in nitrogen atmosphere and aerial oxidation was found to be negligible.

3. Results and discussion

The alkaline hydrolysis of substituted phenyl N,N'-diphenylphosphorodiamidates have been studied in aqueous ethanol and aqueous DMSO. The reaction obeys a good first-order rate expression for the release of phenoxide. The reaction also exhibits a first order dependence on the initial concentrations of sodium hydroxide (table 2). The

Table 1. Melting points of substituted phosphorodiamidates.



X		M. pt (°C)	λ -O Ar (nm)
<i>p</i> -nitro	(Aa)	169–170	400
<i>m</i> -nitro	(Ab)	171–173	390
<i>p</i> -Cl	(Ac)	169–171	300
<i>p</i> -acetyl	(Ad)	175–177	320
<i>p</i> -H	(Ae)	166–168	300

Table 2. Rate constants for the alkaline hydrolysis of *p*-nitrophenyl N,N-phosphorodiamidates (Aa).

10^3 NaOH M	$10^3 k_1 \text{ s}^{-1}$	$k_2 \text{ lit mol}^{-1} \text{ s}^{-1}$
5.0 ^a	1.54	0.303
6.0 ^a	1.87	0.312
11.0 ^a	3.39	0.308
15.0 ^a	4.71	0.314
5.0 ^b	0.290	0.058
10.0 ^b	0.574	0.0574
15.0 ^b	0.870	0.058

second-order rate constants for the various esters in both these solvent media and for different compositions are presented in table 3.

A solvent deuterium isotope effect $k\text{H}_2\text{O}/k\text{D}_2\text{O}$ nearly equal to one has been observed for the *p*-nitrophenyl ester (Aa) in both 50% EtOH and 50% DMSO systems (table 4). The effect of substituents in the leaving phenoxy group has been brought out by a Hammett treatment of the data in table 5 (figure 1). The bimolecular rate constants obey a good Hammett correlation—but only when σ constants rather than σ^- constants are used for *p*-nitro and *p*-acetyl substituents. The Hammett reaction

Table 3. Substituent and solvent effects in the alkaline hydrolysis of aryl phosphorodiamidates.

Compound	% Organic solvent-% H ₂ O	EtOH-H ₂ O	DMSO-H ₂ O (10 k_2 lit mol ⁻¹ s ⁻¹)	HMPT-H ₂ O
Aa	50-50	3.08	0.574	—
	60-40	2.12	0.424	3.82
	70-30	1.68	0.322	2.68
	80-20	1.40	0.255	1.62
Ab	50-50	1.47	0.457	
	60-40	1.20	0.400	
	70-30	0.881	0.266	
	80-20	0.631	0.122	
Ac		10 ⁴ k_2 lit mol ⁻¹ s ⁻¹		
	50-50	44.7	33.1	
	60-40	17.8	14.1	
	70-30	10.0	5.62	
Ad	80-20	3.98	0.316	
	50-50	168	72.4	
	60-40	70.8	32.4	
	70-30	44.7	17.8	
Ae	80-20	20.2	2.24	
		10 ⁵ k_2 lit mol ⁻¹ s ⁻¹		
	50-50	73.5	105	
	60-40	25.1	20.9	
	70-30	11.2	3.87	
	80-20	3.98	0.174	

Temperature—30°C; [ester] = 5×10^{-5} M.

Table 4. Solvent isotope effect in the hydrolysis of *p*-nitrophenyl phosphorodiamidate (Aa)

Solvent composition	10 k_2 lit mol ⁻¹ s ⁻¹	$k\text{H}_2\text{O}/k\text{D}_2\text{O}$
50% EtOH-50% H ₂ O	3.08	0.96
50% EtOH-50% D ₂ O	3.21	
50% DMSO-50% H ₂ O	0.574	0.98
50% DMSO-50% D ₂ O	0.585	
Aa = 5×10^{-5} M NaOD = 1×10^{-2} M		

Table 5. Dependence of Hammett ρ on solvent composition.

% Organic Solvent — % H ₂ O	ρ 30% _{EtOH}	ρ 30% _{DMSO}
50-50	3.6	2.3
60-40	3.7	2.8
70-30	4.0	3.6
80-20	4.5	5.6

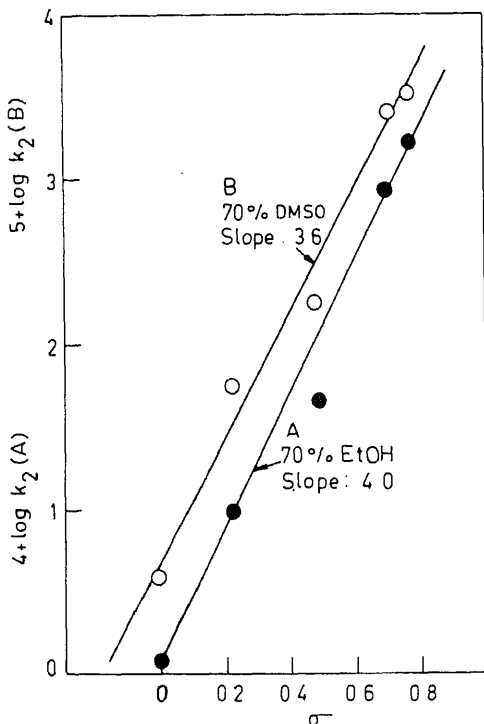
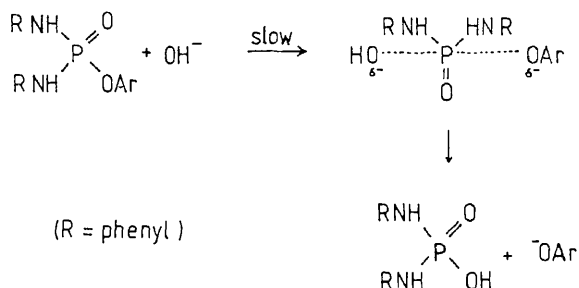


Figure 1. Hammett plot for the alkaline hydrolysis of arylphosphorodiamidates 1. *p*-NO₂ 2. *m*-nitro 3. *p*-COCH₃ 4. *p*-Cl 5. -H.

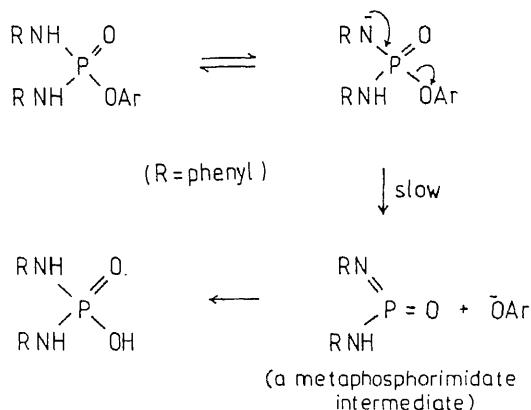
constants are large for these hydrolytic reactions. The magnitude of these values also depends on the nature of the solvent to a large extent. The rate data also fit a Bronsted relationship when the pK_a of the leaving phenols are plotted against $\log k_2$ yielding a value of $\beta = -1.2$ and -1.1 for the reaction in 70% EtOH and 70% DMSO respectively (figure 2).

The foregoing kinetic data for the hydrolysis of the aryl phosphorodiamidates showing a rate dependence on both the substrate and the hydroxide ion concentration

ADDITION - ELIMINATION MECHANISM



ELIMINATION - ADDITION MECHANISM



The experimental observation that the Hammett ρ values for the leaving group are between 2.0 and 5.0 for the hydrolysis indicates, as in the case of phenylmethanesulphonates (Krishnan *et al* 1979) considerable rate-determining cleavage of the P-O bond in the transition state. The transition state for an $\text{S}_{\text{N}}2(\text{P})$ reaction involves little cleavage of the P-OAr bond and one could expect that the rate of hydrolysis will not be subject to any appreciable change on varying the leaving group. The rate-determining step for a E_{1CB} reaction on the other hand is the unimolecular expulsion of the aryloxy groups with the concomitant formation of the $\text{N}=\text{P}$ double bond. The transition state of such a process would have extensive P-OAr bond cleavage and hence substituents in the leaving group can effectively interact with the reaction centre. It is interesting to draw an analogy with the corresponding sulphonate esters where arylbenzenesulphonates have a ρ value of 1.5 (Davy *et al* 1977) for alkaline hydrolysis whereas the arylphenylmethanesulphonates exhibit a ρ value of 4.0 for substitution in the leaving aryloxy group. It may also be pointed out that the high negative β value (-1.25) is

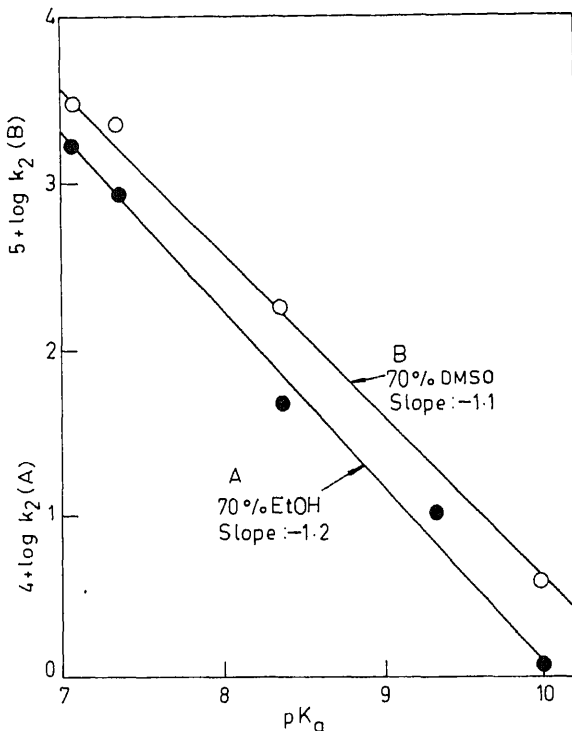


Figure 2. Bronsted plot for the alkaline hydrolysis of arylphosphorodiamidates (Numbers as in figure 1).

greater charge accumulation on the phenolate oxygen in the transition state of the hydrolysis reaction as compared to the ionisation of phenols. The solvent isotope effect of ~ 1 is also indicative of an elimination addition pathway rather than $\text{SN}_2(\text{P})$. Although this criterion has not been well established for a reaction at a phosphorous centre, it is known in the case of carboxylic esters that reactions proceeding by $\text{B}_{\text{AC}}2$ process have $k\text{H}_2\text{O}/k\text{D}_2\text{O}$ values exceeding 1.5 while those that react by a E1CB pathway have values near unity. The observed pronounced reduction in rate on transfer to solvent systems consisting of larger proportions of DMSO (or HMPT) also convincingly establishes that the reaction proceeds via the formation of an ionised substrate, for it has already been established that reactions that proceed by a $\text{B}_{\text{AC}}2$ mechanism exhibit considerable rate acceleration when transferred to dipolar aprotic solvents but hydrolysis by E1CB which generates an anion in the pre-equilibrium step exhibits the opposite effect. Indeed pronounced rate retardations have been noticed in the alkaline hydrolysis of benzoyl acetates (Krishnan *et al* 1979b) pyridyl acetates and indole-2-carboxylates (Rao *et al* 1978) aryl acetates (Chandrashekar and Venkatasubramanian *loc cit*) aryl 4-nitro-phenylmethanesulphonates (Krishnan *et al loc cit*)—situations where an ion is very easily formed in a pre-equilibrium step. The observed retardations in DMSO may be traced directly to the effective solvation of the reactant anion, which is charge-extended and polarisable, by DMSO and this being the ground state of the

The larger question still remains whether the title reaction is indeed a E1CB reaction or an E2 one. An E2 reaction involving the N-H bond of the parent molecule is difficult to demonstrate by isotope effect studies but the pronounced acidity of this hydrogen atom along with the low solvent isotope effect would rule out the operation of such a pathway. Also the large ρ value for the leaving aryloxy group goes against the mechanism. The hydrolysis reactions exhibit high ρ values of 2.3 to 5.6 in DMSO-H₂O mixtures. Such a high sensitivity to the variation in the leaving group is typical of (E1CB)_R reactions (Williams and Douglas 1975).

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Synthesis of some Mannich bases of isatin-3-(4'-phenyl-3'-thiosemicarbazone) and their antibacterial activity

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Abstract. Some Mannich bases of isatin-3-(4'-phenyl-3'-thiosemicarbazone) have been prepared by employing formaldehyde and different secondary amines. These Mannich bases have been characterized on the basis of different physico-chemical evidences. These behave as Lewis-bases and have been estimated accordingly in non-aqueous media. Like some alkaloids they also form the reineckate complexes which serve for their estimation. Antibacterial activity of the synthesized Mannich bases has been studied by employing *Escherichia coli* and *Staphylococcus aureus* as bacterial strains.

Keywords. Mannich bases; reineckate complex; antibacterial activity; *E. coli*; *S. aureus*.

Introduction

A large number of N-Mannich bases of isatin and its 3-thiosemicarbazone have been prepared and tested for antiviral activity (Lucka-Sobstel and Zejc 1972, 1973; Lucka-Sobstel *et al* 1974; Porebska *et al* 1973; Borysiewicz *et al* 1973, 1975; Zgorniak-ovosielska *et al* 1973; Varma and Nobles 1967). Antiviral activity was found to depend on the character of the basic moieties. In this work we have prepared a series of Mannich bases of isatin 3-(4'-phenyl-3'-thiosemicarbazone) in the hope of getting compounds of enhanced antimicrobial activity.

The reaction was carried out by employing equimolar quantities of isatin 3-(4'-phenyl-3'-thiosemicarbazone), dissolved in tetrahydrofuran (THF)-formaldehyde (38 %) solution, and an amine. The secondary amines used as the basic nucleophilic components were dimethylamine, diethylamine, dipropylamine, di-isopropylamine, di-*n*-butylamine, piperidine, morpholine, pyrrolidine, piperazine, *N*-phenyl-piperazine, cyclohexylamine, diphenylamine and dibenzylamine. Isatin forms methylol when its aqueous solution is heated with formaldehyde solution in the presence of potassium carbonate; this suggests that methylol is first formed which is then attacked by amines to give Mannich bases.

Mannich bases are fairly stable in solutions of organic solvents like benzene, alcohol, chloroform and acetone, but get hydrolized when heated with acids and bases. The structure of Mannich bases were confirmed by another route. Isatin was first aminoalkylated followed by condensation with 4-phenyl-3-thiosemicarbazide. The bases thus obtained did not show any depression in melting point upon admixing the bases obtained from direct aminoalkylation of isatin 3-(4'-phenyl-3'-thiosemicarbazone).

acid using 0.5% acetous crystal violet as indicator (violet to bluish-green) (Vogel 1957).

Molecular formulae of the Mannich bases were checked by the standard reineckate-complex method (Beckett and Stenlake 1962). This method depends upon the precipitation of a Mannich base-reineckate complex, which is formed on addition of ammonium reineckate to an acidified solution of the sample.

2. Experimental

Melting points reported are uncorrected and were determined on a Toshniwal melting point apparatus. Infrared spectra were determined on a Perkin Elmer 720 infrared spectrometer as nujol mulls. Nuclear magnetic resonance spectra were recorded on a VARIAN A-60D analytical NMR spectrometer with SiMe_4 as the internal standard. Microanalyses were performed with a Coleman analyser and molecular weights were determined by non-aqueous titration. The Mannich bases were recrystallized from an acetone-ethanol mixture (3:1).

2.1 4-Phenyl-3-thiosemicarbazide (1)

An alcoholic solution of phenyl isothiocyanate (67.6 g, 0.5 M) was treated with a solution of hydrazine hydrate (25.03 g, 0.5 M) to furnish (1) (Pulvermacher *et al* 1893, 1894, from Rodd 1954). The resulting product was filtered and recrystallized from amyl alcohol, m.p. 139° (literature value: 140°) (Tisler *et al* 1956) yield 50.70 g (37.69%).

2.2 Isatin 3-(4'-phenyl-3'-thiosemicarbazone) (1PTS) (2)

4-Phenyl-3-thiosemicarbazide (16.7 g, 0.1 M) dissolved in ethanol (100 ml) was mixed with the solution of isatin (14.7 g, 0.1 M) in water (150 ml) (Halzbecher 1950). The mixture was refluxed on a waterbath for a few minutes. The resulting product obtained after cooling was filtered—m.p. $240\text{--}41^\circ$, yield 25.0 g (84.4%) (found: C-60.81; H-4.06; N-18.86; required for $\text{C}_{15}\text{H}_{12}\text{N}_4\text{OS}$: C-60.79; H-4.07; N-18.90%, ν_{max} (nujol) 3300 (N-H), 1695 (C=O), 1625 (C=N), 1468 cm^{-1} (C=S).

2.3 N-(dimethylaminomethyl) isatin 3-(4'-phenyl-3'-thiosemicarbazone) hydrochloride (3)

To the solution of 1PTS (2.96 g, 0.01 M) in THF (35 ml) were added dimethylamine (0.7 ml, $\approx 0.01\text{ M}$) and 38% aqueous formaldehyde solution (0.8 ml $\approx 0.01\text{ M}$). The reaction mixture was refluxed for five hrs. The separated oil was dissolved in acetone and excess of hydrochloric acid added. The crystals obtained on cooling were filtered—m.p. $162\text{--}63^\circ$, yield 1.8 g (46.27%) (found: C-55.42; H-5.19; N-17.90; mol. wt., 390.20; required for $\text{C}_{18}\text{H}_{20}\text{ClN}_5\text{OS}$: C-55.45; H-5.17; N-17.96%; mol. wt.-389.89), ν_{max} (nujol) 3310 (N-H), 1685 (C=O), 1615 (C=N), 1465 cm^{-1} (C=S).

2.4 N-(diethylaminomethyl) isatin 3-(4'-phenyl-3'-thiosemicarbazone) hydrochloride (4)

To 1PTS (2.96 g, 0.01 M) THF (35 ml) were added diethylamine (1.0 ml, $\approx 0.01\text{ M}$) and 38% aqueous formaldehyde (0.8 ml. $\approx 0.01\text{ M}$). The mixture was refluxed for five hrs.

The oil obtained was dissolved in acetone and excess hydrochloric acid added. The resulting product obtained after cooling was filtered—m.p. 87° , yield 1.5 g (35.9%) (found: C-57.43; H-5.80; N-6.72; mol. wt.-416.32; required for $C_{20}H_{24}ClN_5OS$; C-57.47; H-5.79; N-6.75%; mol. wt.-417.94), $\nu_{\max}$ (nujol) 3305 (N-H), 1685 (C=O), 1612 (C=N), 1465 cm^{-1} (C=S).

5 *N*-(dipropylaminoethyl) isatin 3-(4'-phenyl-3'-thiosemicarbazone) hydrochloride (5)

To a solution of IPTS (2.96 g, 0.01 M) in THF (35 ml) were added dipropylamine (1.4 ml, 0.01 M) and 38% formaldehyde solution (0.8 ml, ≈ 0.01 M). The reaction mixture was refluxed on a water bath for about five hrs. The oil obtained was dissolved in acetone and excess hydrochloric acid added. After cooling the product obtained was filtered—m.p. $111-13^{\circ}$, yield 1.2 g (26.96%) (found: C-59.31; H-6.35; N-15.76; mol. wt.-446.25; required for $C_{22}H_{28}ClN_5OS$: C-59.24; H-6.33; N-15.70%; mol. wt.-445.99), $\nu_{\max}$ (nujol) 3300 (N-H), 1685 (C=O), 1610 (C=N), 1643 cm^{-1} (C=S).

6 *N*-(di-isopropylaminomethyl) isatin 3-(4'-phenyl-3'-thiosemicarbazone) hydrochloride (6)

IPTS (2.96 g, 0.01 M) dissolved in THF (35 ml) was treated with a mixture of di-isopropylamine (1.4 ml, ≈ 0.01 M) and 38% formaldehyde solution (0.8 ml, ≈ 0.1 M). The reaction mixture was refluxed for two hrs. on a water bath till half the solvent evaporated. The separated oil was dissolved in acetone and excess hydrochloric acid added. The oil obtained again was crystallized from methanol—m.p. 161° (decomposition-D), yield 1.6 g (35.96%) (found: C-59.31; H-6.37; N-15.53; mol. wt.-443.65; required for $C_{22}H_{28}ClN_5OS$: C-59.24; H-6.33; N-15.70% mol. wt.-445.99), $\nu_{\max}$ (nujol) 3300 (N-H), 1690 (C=O), 1616 (C=N), 1468 cm^{-1} (C=S).

7 *N*-(di-isobutylaminomethyl) isatin 3-(4'-phenyl-3'-thiosemicarbazone) hydrochloride (7)

To a solution of IPTS (2.96 g, 0.01 M) in THF (35 ml) were added diisobutylamine (1.8 ml, 0.01 M) and a solution of 38% formaldehyde (0.8 ml, 0.01 M). The resulting reaction mixture was refluxed on a water bath for five hrs. The separated oil was dissolved in acetone and excess hydrochloric acid added. The crystals obtained on cooling were filtered, m.p. 230° (D), yield 0.5 gm (10.54%) (found: C-60.76; H-6.85; N-14.82, mol. wt.-475.26; required for $C_{24}H_{32}ClN_5OS$: C-60.80; H-6.80; N-14.77%, mol. wt.-474.04).

8 *N*-(Piperidinomethyl) isatin 3-(4'-phenyl-3'-thiosemicarbazone) hydrochloride (8)

To a solution of IPTS (2.96 g, 0.01 M) in THF (35 ml) were added piperidine (1.0 ml, 0.01 M) and 38% formaldehyde (0.8 ml, ≈ 0.01 M). The reaction mixture was refluxed on a water bath for five hrs. The oil obtained was dissolved in acetone and excess hydrochloric acid added. The crystals obtained on cooling were filtered—m.p. 105° , yield 1.0 g (23.26%) (found: C-58.55; H-5.70; N-16.02; mol. wt.-428.25; required for $C_{21}H_{24}ClN_5OS$: C-58.65; H-5.62; N-16.28%, mol. wt.-428.96).

9 *N*-(Morpholinomethyl) isatin-3-(4'-phenyl-3'-thiosemicarbazone) (9)

To a solution of IPTS (2.96 g, 0.01 M) in THF (35 ml) were added morpholine (0.9 ml

C₂₀H₂₁N₅O₂S: C-60.47; H-5.31; N-17.71, mol. wt.-395.46).

2.10 *N*-(Pyrrolidinomethyl) isatin 3-(4'-phenyl-3'-thiosemicarbazone) hydrochloride (10)

IPTS (2.96 g, 0.01 M) was dissolved in THF (35 ml) and pyrrolidine (0.9 ml, $\approx$ 0.01 M) and 38 % formaldehyde (0.8 ml, $\approx$ 0.01 M) were added to it. The resulting mixture was refluxed on a water bath for about five hrs. The oil obtained was dissolved in acetone and excess hydrochloric acid added. The product separated after cooling was filtered, m.p. 81°, yield 0.4 g (9.63 %) (found: C-57.63; H-5.23; N-16.45; mol. wt.-416.23; required for C₂₀H₂₂ClN₅OS: C-57.75; H-5.33; N-16.83 %, mol. wt.-415.93), $\nu_{\max}$ (nujol) 3300 (N-H), 1685 (C=O), 1615 (C=N), 1465 cm⁻¹ (C=S).

2.11 *Bis N-N'*-piperazino-methyl-isatin-3-(4'-phenyl-3'-thiosemicarbazone) (11)

To a solution of IPTS (2.96 g, 0.01 M) in THF (35 ml) were added piperazine (1.0 g, $\approx$ 0.005 M) and 38 % formaldehyde solution (0.8 ml, $\approx$ 0.01 M). The reaction mixture was refluxed on a water bath for 15 minutes. The product separated during refluxing was filtered—m.p. 209–10°, yield 3.0 g (42.73 %) (found: C-61.46; H-4.82; N-19.85; mol. wt.-700.05; required for C₃₆H₃₄N₁₀O₂S₂: C-61.52; H-4.88; N-19.93 %, mol. wt.-702.82), $\nu_{\max}$ (nujol) 3295 (N-H), 1692 (C=O), 1615 (C=N), 1465 cm⁻¹ (C=S).

2.12 *N*-(*N'*-phenyl-piperazinomethyl) isatin 3-(4'-phenyl-3'-thiosemicarbazone) (12)

To a solution of IPTS (2.96 g, 0.01 M) in THF (35 ml) were added *N*-phenyl piperazine (1.6 g, $\approx$ 0.01 M) and 38 % formaldehyde solution (0.8 ml, $\approx$ 0.01 M). The reaction mixture was refluxed for four hrs. on a water bath two-thirds of the solvent was evaporated. It was cooled in the refrigerator overnight and the separated crystals were filtered out—m.p. 154°, yield 1.3 g (27.65 %) (found: C-66.16; H-5.47; N-17.58; mol. wt.-468.36; required for C₂₆H₂₆N₆OS: C-66.36; H-5.57; N-17.86 %, mol. wt.-470.57), $\nu_{\max}$ (nujol) 3305 (N-H), 1690 (C=O), 1615 (C=N), 1470 cm⁻¹ (C=S). NMR δ (CDCl₃) 2.8–3.4 may be due to the eight methylene protons of the piperazine ring. A sharp singlet at 4.6 may be assigned to the two methylene protons between the two nitrogen atoms and a multiplet at 6.9–7.9 is due to fourteen aromatic protons. A peak at 9.6 δ which disappeared in D₂O exchange may be due to the two N-H protons of the thiosemicarbazide moiety.

2.13 *N*-(dicyclohexylaminomethyl) isatin 3-(4'-phenyl-3'-thiosemicarbazone) hydrochloride (13)

IPTS (2.96 g, 0.01 M) was dissolved in THF (35 ml). Dicyclohexylamine (2.0 ml, $\approx$ 0.01 M) and 38 % formaldehyde solution (0.8 ml, $\approx$ 0.01 M) were added to it. The mixture was refluxed on a water bath for nine hrs., half of the solvent was evaporated. After cooling the oil obtained was dissolved in acetone and hydrochloric acid gas was passed through it. The oil obtained got crystallized when more acetone was added, m.p.-285° (D), yield 1.0 g (19.01 %) (found: C-63.20; H-6.84; N-13.41; mol. wt.-525.15 required for C₂₈H₃₆ClN₅OS: C-63.92; H-6.90; N-13.31 %, mol. wt.-526.12), $\nu_{\max}$ (nujol) 3300 (N-H), 1690 (C=O), 1615 (C=N), 1465 cm⁻¹ (C=S).

diphenylamine (1.5 g, ≈ 0.01 M) and 38 % formaldehyde solution (0.8 ml, ≈ 0.01 M) were mixed to a solution of IPTS (2.96 g, 0.01 M) dissolved in THF (35 ml). The resulting mixture was refluxed on a water bath for an hr, half the solvent evaporated. On cooling the crystals separated and they were filtered—m.p.-237–39 (D), yield 1.7 g (35.60 %) (found: C-70.31; H-4.81; N-14.12; mol. wt.-479.32; required for $C_{28}H_{23}N_5OS$: C-70.42; H-4.85; N-14.66 %; mol. wt.-477.55), $\nu_{\max}$ (nujol) 3300 (N-H), 1690 (C=O), 1620 (C=N), 1465 cm^{-1} (C=S).

15 *N*-(Dibenzylaminomethyl) isatin 3-(4'-phenyl-3'-thiosemicarbazone) hydrochloride (15)

To a solution of IPTS (2.96 g, 0.01 M) in THF (35 ml) were added dibenzylamine (2.0 ml, ≈ 0.01 M) and 38 % formaldehyde solution (0.8 ml, ≈ 0.01 M). The reaction mixture was refluxed on a water bath for about fifteen hrs., half the solvent evaporated. The oil obtained was dissolved in dry ether and hydrogenchloride gas was passed through it. The oil again obtained got crystallized when shaken with acetone—m.p.-208–10°, yield-1.1 g (20.29 %) (found: C-66.51; H-5.22; N-13.01; mol. wt.-541.05; required for $C_{30}H_{28}ClN_5OS$: C-66; H-5.21; N-12.92 % mol. wt.-542.07), $\nu_{\max}$ (nujol) 3300 (N-H), 1590 (C=O), 1615 (C=N), 1475 cm^{-1} (C=S).

Screening for antibacterial activity

Antibacterial activity of the synthesized Mannich bases has been studied by employing *Escherichia coli* and *Staphylococcus aureus* as bacterial strains. The paper disc diffusion method (Cruickshank *et al* 1965) was employed for the evaluation of the antibacterial

Table 1. Antibacterial activity of Mannich bases of isatin 3-(4'-phenyl-3'-thiosemicarbazone)

Compound		Antibacterial activity	
		Diameter of zone of inhibition (mm)	
Name	Number	<i>E. coli</i>	<i>S. aureus</i>
N-(dimethylaminomethyl) IPTS-HCl	1	15	12
N-(diethylaminomethyl) IPTS-HCl	2	—	9
N-(di- <i>n</i> -propylaminomethyl) IPTS-HCl	3	16	14
N-(di- <i>i</i> -propylaminomethyl) IPTS-HCl	4	7	8
N-(di- <i>i</i> -butylaminomethyl) IPTS-HCl	5	7	—
N-(piperidinomethyl) IPTS-HCl	6	8	7
N-(morpholinomethyl) IPTS	7	9	16
N-(pyrrolidinomethyl) IPTS-HCl	8	8	8
N,N'-piperazino-bis-(methyl IPTS)	9	—	—
N-(N-phenylpiperazinomethyl) IPTS	10	9	7
N-(dicyclohexylaminomethyl) IPTS-HCl	11	14	12
N-(diphenylaminomethyl) IPTS	12	14	9
N-(dibenzylaminomethyl) IPTS-HCl	13	12	11

activity. A heavy suspension of the inoculum was streaked or smeared over the surface of the agar media. Bactosensitivity paper discs of 6.25 mm diameter, containing drugs, (0.25 mg/ml) were placed on the medium suitably spaced apart full aseptic precautions. The plates were incubated at 37°C for 24 hours and the zone of inhibition was measured.

The results of the antibacterial screening of the Mannich bases has been summarised in table 1. It is evident from the results that the majority of Mannich bases showed some measurable zone of bacterial inhibition. The compounds N-(dimethylaminomethyl)-isatin-3-(4'-phenyl-3'-thiosemicarbazone)-hydrochloride; N-(di-n-propylaminomethyl)-isatin-3-(4'-phenyl-3'-thiosemicarbazone)-hydrochloride; N-(morpholinomethyl)-isatin-3-(4'-phenyl-3'-thiosemicarbazone); N-(dicyclohexylaminoethyl)-isatin-3-(4'-phenyl-3'-thiosemicarbazone)-hydrochloride; N-(diphenylaminoethyl)-isatin-3-(4'-phenyl-3'-thiosemicarbazone) and N-(dibenzylaminomethyl)-isatin-3-(4'-phenyl-3'-thiosemicarbazone)-hydrochloride have marked activity.

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Kinetics of reaction of ethyl bromoacetate with substituted phenoxyacetate ions

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Abstract. The reaction of ethyl bromoacetate with substituted phenoxyacetate ions in 90 % aqueous acetone is found to follow total second order kinetics, first order in each reactant. The reaction is accelerated by electron-releasing and retarded by electron-withdrawing substituents in the phenoxyacetate ion. The reaction shows an excellent Hammett fit, $\rho = -0.242$ at 40°C. The attenuation ratio (π_2) is found to be 0.695, indicating the damping effect of the oxymethylene group $-\text{O}-\text{CH}_2-$. A satisfactory Brönsted correlation is observed for the reaction, $\alpha = 1.1$ at 25°C. The isokinetic relationship is obeyed in the present reaction series, β (isokinetic temperature) = 334 K.

Keywords. Substituent effects; damping effect of oxymethylene group; ion pairs.

Introduction

Molecular nucleophilic substitution reactions have been of immense fascination to mechanistic organic chemists in recent decades, especially because of the possibility that they afford correlation of substituent effects on reaction rates with the aid of the Hammett equation or its modifications (Bunnett and Zahler 1951; Hughes 1951; Bunnett 1958; Kosower 1968; Gould 1959). α -Haloketones and α -haloesters have been found to be considerably reactive towards nucleophiles and have been employed by numerous workers for such studies. Kinetics of the reactions of phenacyl bromide, substituted phenacyl bromides and substituted ω -bromoacetophenones with various types of nucleophiles have been studied (Mohanty *et al* 1967; Mishra *et al* 1973; Manthakrishna Nadar *et al* 1975, 1976, 1977; Srinivasan *et al* 1981a). Quite recently, detailed kinetic studies on the reaction of ethyl bromoacetate (EBA) with substituted phenoxyacetate ions (Srinivasan *et al* 1981b) and *trans*-cinnamate ions (Srinivasan *et al* 1982) are reported. Literature does not, however, record any extensive study of the reaction of this α -haloester with substituted phenoxyacetate ions. This prompted us to undertake the title investigation.

Experimental

Ethyl bromoacetate (Fluka) of high purity was used for the study. The substituted phenoxyacetic acids were prepared by treatment of the sodium salt of the appropriately substituted phenols with monochloroacetic acid (Vogel 1948) and purified by crystallization. Acetone used was of AR grade.

The reaction of EBA with phenoxyacetate ions was studied in 90 % acetone – 10 %

water mixtures at 30°, 35° and 40°C. The reaction was followed by withdrawing suitable aliquots of the reaction mixture at regular intervals into a solution of nitric acid and a definite, known excess of standard silver nitrate solution and titrating the excess, unconsumed silver nitrate against standard ammonium thiocyanate solution using ferric alum indicator.

The rate constants were calculated using the second order equation

$$k_2 = \frac{1}{t} \cdot \frac{x}{a(a-x)},$$

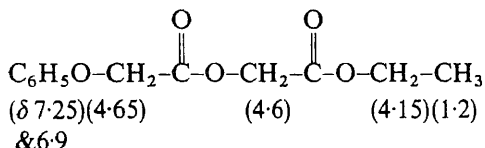
when the initial concentrations of the two reactants were equal, or the other second-order expression

$$k_2 = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)},$$

where a is the initial concentration of EBA, b the initial concentration of the phenoxyacetate ion and x the concentration of bromide ion formed in time t (sec), when the initial concentrations of the two reactants were unequal. The reaction was studied at three different temperatures and the E_a values were calculated from the slopes of the Arrhenius plots of $\log k_2$ versus T^{-1} . Using these E_a values, the value of $\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\Delta G^\ddagger$ were evaluated.

2.1 Product analysis

In order to isolate the product of the reaction, sodium phenoxyacetate and EBA were allowed to react in equal volumes in equimolar solutions in 90% aqueous acetone for two days and the solvent removed by evaporation under atmospheric pressure. The residual liquid was extracted with ether, dried (over Na_2SO_4) and relieved of ether by evaporation. A pleasant-smelling liquid was left behind. Its IR (film: [1750 (ester C=O stretching), 1020–1380 cm^{-1} (intense multiple bands, C–O stretching)]) and PMR [(90 MHz, CDCl_3 : δ 7.25 (t, 2H, $J = 7.5$ Hz), 6.9 (t, 3H, $J = 7.5$ Hz), 4.65 (s, 2H), 4.6 (s, 2H), 4.15 (q, 2H, $J = 6.5$ Hz) and 1.2 (t, 3H, $J = 6.5$ Hz))] spectra are consistent with structure I with the assignment of signals as shown.

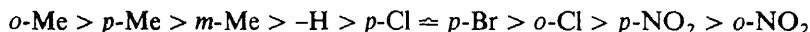


I

3. Results and discussion

3.1 Kinetic order and substituent effects

where X is a substituent in the benzene ring. The second order rate constants and activation parameters for the reaction of EBA with 9 substituted phenoxyacetate ions are given in table 1. The kinetic data unmistakably indicate rate acceleration by electron-releasing and retardation by electron-withdrawing substituents and dependence of the reaction rate on the electron density on the oxygen atom of the phenoxyacetate anion. The overall order of reactivity is



and is analogous to those reported earlier by other workers (Mohanty *et al* 1967; Mishra *et al* 1973; Ananthakrishna Nadar *et al* 1976, 1977; Srinivasan *et al* 1981a) and is readily explicable on the basis of the inductive, mesomeric and/or hyperconjugative effects of the substituent. It is pertinent to note that the phenoxyacetate ion reacts faster than the benzoate ion (Srinivasan *et al* 1981b), obviously due to the fact that the phenoxy group is a stronger electron-withdrawing group than the phenyl group.

The reaction shows an Hammett fit as the plots of $\log k_2$ of the *m*- and *p*-substituted phenoxyacetate ions against the corresponding σ values were quite linear. The slopes of these plots yielded ρ values of -0.242 (at 40°C , $r = 0.986$), -0.265 (at 35°C , $r = 0.997$) and -0.296 (at 30°C , $r = 0.990$). The negative sign of ρ signifies that the reaction is facilitated by electron release from the benzene ring towards the reaction centre. The decline in the value of ρ with rise of temperature is expected since σ is temperature dependent. It has been shown that in simple cases ρ should vary as $1/T$ (Leffler 1955, 1957; Fischer and Vaughan 1957).

It is instructive to compare the ρ value in the present case with that for the similar reaction of EBA with benzoate ions. Since ρ has been reported for the latter to be -0.381 at 35°C by Srinivasan *et al* (1981b), we find that the substituent effect is much less pronounced in the present case. This is in keeping with the general observation that the effect of a substituent in the benzene ring on a particular kind of reaction in a side chain decreases with increasing length of the chain (More O'Ferrall and Miller 1964; Jaffé 1953; Trachetenberg and Odian 1958; Ananthakrishna Nadar and Petchinatha Pillai 1981). The attenuation ratio $\pi_z (= \rho/\rho_0)$ works out to $(-0.265/-0.381) = 0.695$ at

Table 1. Second order rate constants and activation parameters for the reaction of phenoxyacetate ions with ethyl bromoacetate in 90% aq. acetone.

Substituent	$10^3 \times k_2 \text{ M}^{-1} \text{ s}^{-1}$			E_a k cal/ mole	$\Delta H^\ddagger$ k cal/ mole	$\Delta S^\ddagger$ cal/mole/ deg	$\Delta G^\ddagger$ k cal/ mole
	30°C	35°C	40°C				
Me	0.586	0.905	1.370	16.02	15.42	-22.46	22.23
Me	0.542	0.872	1.350	17.39	16.79	-18.10	22.27
<i>m</i> -Me	0.517	0.812	1.260	16.78	16.18	-20.20	22.30
H	0.463	0.760	1.230	18.46	17.86	-14.88	22.37
Cl	0.436	0.686	1.030	16.02	15.42	-23.05	22.40
Br	0.429	0.667	1.020	16.95	16.35	-20.01	22.41
Cl	0.308	0.517	0.852	19.36	18.76	-12.72	22.61
NO ₂	0.285	0.487	0.812	19.41	18.81	-12.71	22.66
NO ₂	0.249	0.444	0.762	20.80	20.20	-8.39	22.74

transmission of the electronic effects through the group F in Ar-F-COOH compared with that of similar benzoic acid derivatives. It measures in the present case the weakening of the effect of a substituent by the interposition of the oxymethylene group, $-\text{O}-\text{CH}_2-$. The magnitude of the damping effect of the oxymethylene bridge is thus revealed.

The applicability of the Brönsted equation was then tested by plotting $\log k_2$ (at 25°C) for the reaction of the *m*- and *p*-substituted phenoxyacetate ions against the pK_a of the corresponding conjugate acids. A good straight line was obtained and the Brönsted coefficient α in the present case was found to be 1.1 ($r = 0.954$), indicating an excellent fit with the Brönsted equation. The positive value of α is in accord with the expectation for a bimolecular nucleophilic substitution reaction, i.e., the rate increases with increasing basicity of the nucleophile. The rather high value of α signifies that there is substantial bond formation between the nucleophile and the reaction centre in the present case.

3.2 Temperature influence

The temperature influence on this reaction series has been studied in the range 30 to 40°C and the activation parameters evaluated as indicated earlier.

Inspection of the data on activation parameters indicates that electron-releasing substituents lower E_a while electron-withdrawing substituents increase it since the former lead to increased nucleophilicity and the latter to reduced nucleophilicity of the phenoxyacetate ion. However, the E_a values do not correctly or quantitatively reflect the electronic effect of the substituents. The entropy of activation is negative in all the cases, as expected for a bimolecular nucleophilic substitution reaction in which there is increased steric crowding in the transition state. The constancy of the $\Delta G^\ddagger$ values in all the cases points to the operation of the same mechanism throughout the series. This is a consequence of the variation in $\Delta H^\ddagger$ being compensated by the variation in $\Delta S^\ddagger$. The isokinetic relationship $\Delta H^\ddagger = \Delta H_0^\ddagger + \beta \Delta S^\ddagger$ is found to hold good in the present reaction series and a plot of $\Delta H^\ddagger$ against $\Delta S^\ddagger$ is linear and the slope β (isokinetic temperature) = 334 K ($r = 0.998$).

3.3 Solvent influence

With a view to studying the effect of variation in solvent composition on the rate of the reaction, the reaction has been studied in acetone-water mixtures of various compositions. The reaction is found to become slower with increasing percentage of water. For example, at 40°C under the conditions, $[\text{EBA}] = 0.02\text{ M} = [\text{phenoxyacetate ion}]$, $10^3 k_2$ decreases from 1.230 to $0.352\text{ M}^{-1}\text{ sec}^{-1}$ when % water was increased from 10 to 25 . This is as expected for a reaction in which the negative charge which was confined to the phenoxyacetate ion prior to reaction is dispersed over a somewhat larger area in the transition state. It is also possible that this result is due to greater solvation of the anionic nucleophile via hydrogen bonding by the protic component (water) of the medium resulting in diminished nucleophilicity of the anion.

3.4 Effect of [sodium phenoxyacetate] on rate: evidence for ion pairs

It is observed that the reaction velocity decreases with increasing concentration of the sodium phenoxyacetate. For example, at 40°C under the conditions, $[\text{EBA}] = 0.02\text{ M}$ in

90% acetone-water mixture, $10^3 k_2$ decreases from 2.11 to $1.23 \text{ M}^{-1} \text{ sec}^{-1}$ when [sodium phenoxyacetate] is increased from 0.0025 to 0.0200 M. This is not surprising since acetone is a poorly dissociating medium and it would be reasonable to suppose that the salt is not completely dissociated in 90% aqueous acetone. The phenoxyacetate and the sodium ions may be held together by electrostatic attraction to form ion pairs. At high concentrations of the salt this phenomenon would become more pronounced, causing a decline in the rate.

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Synthesis and characterization of α -oximino- β -thiosemicarbazino-acetoacetaryl amides and their cyclized product vicinal triazoles

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Abstract. Several α -oximino- β -thiosemicarbazones of acetoacetaryl amides have been synthesized by condensing thiosemicarbazide and α -oximinoacetoacetaryl amides. α -Oximino- β -thiosemicarbazinoacetoacetaryl amides are cyclized employing thionyl chloride or acetic anhydride/sodium acetate to give N-aryl 4-methyl-2-thiocarbamido-1,2,3-triazole-5 carboxylic acid amide. The compounds reported herein are characterized by UV, IR and micro-analytical data.

Keywords. α -Oximino- β -thiosemicarbazones of acetoacetaryl amides; vicinal triazoles; UV and IR studies.

1. Introduction

α -Oximinohydrazones have been shown to possess biological activity by several investigators (Giammanco 1961; Misra and Verma 1962) by virtue of the presence of the $-\text{CONH}-\text{N}=\text{C}-$ group and the $=\text{NOH}$ group, which impart antiparasitic, fungicidal and bactericidal properties to such compounds. α -Oximino- β -hydrazones of acetoacetaryl amides have been shown (Patel and Mankad 1968; Patel *et al* 1975) to be utilized quantitatively for the estimation of transition metal ions such as Ni and Pd, either alone or in the presence of other metals. Cyclization of oximinohydrazones affords vicinal triazoles (Rupput and Nilsson 1961). Several investigators (Guglielmo *et al* 1973; Geigy 1972; Fritz *et al* 1973; David *et al* 1972; Osamu *et al* 1972) have reported the synthesis of *vis*-triazoles from oxime hydrazones and shown to possess whitening property and also pharmacological activity.

In view of the above survey, it was considered worthwhile to undertake a systematic study of the preparation and characterization of α -oximino- β -thiosemicarbazones of acetoacetaryl amides and their cyclized products vicinal triazoles.

2. Experimental

All the chemicals used are of analytical grade. α -Oximinoacetoacetaryl amides have been prepared (Knorr 1887) and crystallized from aqueous ethanol.

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carried out by treating *o*-oximinoacetoacetaryl amides in ethanol with semicarbazide in equimolar proportions and adding a few drops of concentrated HCl. On keeping for 1–3 hrs., the product separating was filtered and crystallized from aqueous ethanol. In all the cases the yield obtained was in the range of 75 to 80 %. The analytical results are recorded in table 1.

2.2 Preparation of vicinal triazoles

α -Oximino- β -thiosemicarbazones of acetoacetaryl amides (0.5 gm) were mixed with excess of freshly distilled thionyl chloride (about 20 ml). The contents were refluxed at 80–90°C for 3 hrs. Excess thionyl chloride was distilled off at atmospheric pressure while traces were removed by distillation *in vacuo* after adding benzene and petroleum ether successively. The semisolid mass solidified on trituration with dry ether. Ether was allowed to evaporate and the fine solid powder obtained was dried at 50–60°C and then kept in a vacuum desiccator till the odour of thionyl chloride disappeared. The compounds thus obtained were recrystallized from ethanol and are listed in table 2.

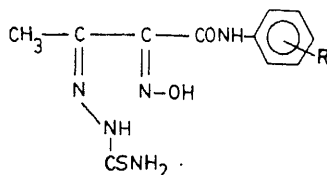
The 2,4,5-trisubstituted 1,2,3-triazoles reported here and prepared by the above method were also synthesized by the action of acetic anhydride (about 20 ml)/sodium acetate (about 0.2 gm) on the corresponding α -oximinothiosemicarbazones (about 0.1 to 0.2 gm) at the reflux temperature of acetic anhydride for 3 hrs, followed by the distillation of excess acetic anhydride and pouring of the residual reaction mass onto ice. The solid products separated in each case were crystallized from ethanol. The melting points of the products were found to be the same as those prepared by the above method.

2.3 Physical measurements

Nitrogen content were estimated by micro Duma's method. uv measurements were carried out using ethanol as a solvent. IR spectra in the form of their KBr pellets were recorded (400 cm^{-1} to 4000 cm^{-1}).

3. Results and discussion

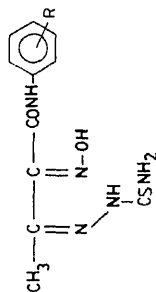
α -Oximino- β -thiosemicarbazinoacetoacetaryl amides have been assigned anti-configuration (Patel and Mankad 1964) as



where R = H, *o*-CH₃, *p*-CH₃, *o*-Cl, *m*-Cl, *p*-Cl, *o*-OCH₃, *p*-OCH₃, 2:4 (CH₃)₂.

Table 1 shows the uv data for oximino thiosemicarbazones. The absorption pattern was characterized by the presence of two bands around 235–255 nm and 304–305 nm.

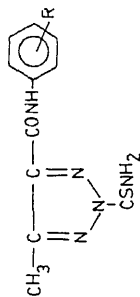
Table 1. Analytical and uv spectral data of α -oximino- β -thiosemicarbazones of acetoacetyl/aramides.



No. R	Molecular formula	M.P.°C (D)	% Nitrogen		$\lambda_{\max}$ (nm)	(log $\epsilon_{\max}$)
			Literature	Found		
1 H	C ₁₁ H ₁₃ O ₂ N ₃ S	176-7	25.10	23.15	305	(4.4)
2 <i>o</i> -CH ₃	C ₁₂ H ₁₃ O ₂ N ₃ S	151-2	23.88	23.84	245	(4.2)
3 <i>p</i> -CH ₃	C ₁₂ H ₁₃ O ₂ N ₃ S	175	23.88	23.95	304	(4.4)
4 <i>o</i> -Cl	C ₁₁ H ₁₂ O ₂ N ₃ SCl	160-2	22.33	22.10	235	(4.1)
5 <i>m</i> -Cl	C ₁₁ H ₁₂ O ₂ N ₃ SCl	180	22.33	22.20	305	(4.4)
6 <i>p</i> -Cl	C ₁₁ H ₁₂ O ₂ N ₃ SCl	170	22.33	22.46	245	(4.3)
7 <i>o</i> -OCH ₃	C ₁₂ H ₁₃ O ₃ N ₃ S	158-9	22.65	22.60	305	(4.5)
8 <i>p</i> -OCH ₃	C ₁₂ H ₁₃ O ₃ N ₃ S	171	22.65	22.70	250	(4.4)
9 2:4 (CH ₃) ₂	C ₁₃ H ₁₇ O ₂ N ₃ S	187-9	22.81	22.90	305	(4.4)
					238	(4.1)

D—decomposed.

Table 2. Analytical and uv spectral data of vicinal triazoles.



No.	R	Molecular formula	M.P.°C (D)	Colour	% Nitrogen		$\lambda_{\max}$ (nm)	$(\log \epsilon_{\max})$
					Literature	Found		
1	H	$C_{11}H_{11}ON_5S$	160	Reddish yellow	26.82	26.46	275	(5.8)
2	<i>o</i> -CH ₃	$C_{12}H_{13}ON_5S$	80	Buff yellow	25.46	25.51	270	(5.4)
3	<i>p</i> -CH ₃	$C_{12}H_{13}ON_5S$	154	Yellow	25.46	25.73	265	(5.8)
4	<i>o</i> -Cl	$C_{11}H_{10}ON_5SCl$	230	Dark yellow	23.69	23.27	268	(5.6)
5	<i>m</i> -Cl	$C_{11}H_{10}ON_5SCl$	155	Yellow	23.69	23.88	268	(5.8)
6	<i>p</i> -Cl	$C_{11}H_{10}ON_5SCl$	140	Yellow	23.69	23.99	270	(5.6)
7	<i>o</i> -OCH ₃	$C_{12}H_{13}O_2N_5S$	170	Lemon yellow	24.05	23.65	260	(5.7)
8	<i>p</i> -OCH ₃	$C_{12}H_{13}O_2N_5S$	90	Dark yellow	24.05	23.69	275	(5.6)
9	2:4(CH ₃) ₂	$C_{13}H_{15}ON_5S$	225	Light yellow	24.23	24.80	262	(5.4)

D—decomposed.

IR spectral data of α -oximino- β -thiosemicarbazones of acetoacetylarnides and their cyclized product vicinal triazoles.

	OH Stretch	C=N Stretch	N-O Stretch	C=S Stretch	Triazole ring vibration	Ring breathing and C-H in plain vibration	-NH-		
							I	II	III
300 s	2833 s	1610 vs	960 vs	1083 s	—	—	1681 vs, 1612	1555 vs	1325 m
—	—	1615 s	—	1330 s	1240 s, 1160 s	1130 s, 1070 m, 905 s, 875 s	1665 s	1540 vs	1300 s
300 s	2857 s	1600 s	962 s	1064 s	—	—	1670 s, 1653 s	1520 s, 1527 s	1315 vs
—	—	1600 s	—	1360 s	1250 s, 1170 s	1050 s, 1130 s, 1070 s, 900 s	1675 s	1540 s	1300 s
300 s	2874 s	1600 s	964 vs	1064 s	—	—	1670 vs	1555 s	1300 vs
—	—	1605 s	—	1325 s	1255 s, 1245 m	1130 s, 1050 s, 990 s, 900 s	1675 s	1540 s	1300 vs
33 s	2890 w	1603 s	960 vs	1057 s	—	—	1680 s, 1658 m	1546 s, 1520 s	1300 vs
—	—	1600 s	—	1330 s	1220 s, 1190 s, 1160 m	1130 s, 1075 s, 1010 m, 920 s	1690 s	1530 s	1300 s
375 s	2885 s	1610 vs	960 vs	1058 s	—	—	1672 vs	1555 s	1300 vs
—	—	1605 s	—	1320 s	1245 s, 1180 s, 1160 s	1130 s, 1075 m, 1010 s, 920 s	1675 s	1540 s	1310 s
380 s	2833 s	1605 vs	952 vs	1050 m	—	—	1695 s	1543 s	1300 vs
—	—	1610 s	—	1325 s	1260 m, 1225 s, 1180 s	1125 s, 1070 s, 1030 s, 990 m, 900 s	1675 s	1550 s	1300 s
372 s	2874 w	1610 vs	966 vs	1058 s	—	—	1672 vs, 1658 s	1550 s	1300 vs
—	—	1605 s	—	1330 m	1250 s, 1220 s, 1180 m	1130 s, 1100 m, 1050 s, 1015 s,	1670 s	1550 s	1300 vs
380 s	2890 s	1610 vs	963 vs	1057 m	—	990 m	1672 vs	1550 s	1300
—	—	1600 s	—	1360 m	1240 s, 1200 m, 1170 s	1090 s, 1015 m, 990 s, 890 s	1680 vs	1535 s	1320 s
375 s	2890 s	1600 s	960 vs	1057 m	—	—	1667 s	1545 m	1290 vs
—	—	1600 s	—	1360 m	1260 m, 1220 s, 1160 s	1140 s, 1060 m, 1040 s, 990 s	1680 s	1545 s	1300 vs

represent the α -oximinothiosemicarbazones from table I, those with superscript c are the corresponding triazoles; s = strong, vs = very strong, ad.

The uv spectra of acetoacetaryl amides and thiosemicarbazide moieties in ethanol show a maxima around 245–252 nm and 230–240 nm respectively. On comparing these data with those given in table 1 it is revealed that the band at 303–305 nm can be assigned to the new chromophoric system $[N=C-C(=N)-C=O]$ and shows a bathochromic displacement to the extent of 53–64 nm (compared to the parent amide $\lambda_{\max}$ 245–252 nm) with increase in absorption intensity. The band observed at 235–255 nm is due to the thiosemicarbazide moiety which shows an increase in intensity compared to acetoacetaryl amides (Patel and Mankad 1964).

The IR spectra of α -oximino- β -thiosemicarbazinoacetoacetaryl amides have exhibited bands in the region $3100\text{--}3400\text{ cm}^{-1}$ which may be attributed to free NH_2 of carbazide moiety, bonded NH of amide and OH of oxime stretchings (Hadzi and Jan 1965). The bands around 1600 cm^{-1} and $940\text{--}970\text{ cm}^{-1}$ are assigned to $C=N$ and $N-O$ stretchings respectively (Ungnado *et al* 1963). The secondary amide and $C-Cl$ stretching vibrations are located at their usual positions (Rao 1961).

The 2,4,5-trisubstituted vicinal triazoles prepared here do not show a tendency to form metal complexes with transition metal ions which indicates the absence of free $=N-OH$ and the formation of a triazole ring. It is suggested that under reaction conditions the compounds undergo a steric change from anti-to amphi-configuration (δ) and then follow the cyclodehydration.

The uv spectral data of 2,4,5-trisubstituted 1,2,3-triazoles (table 2) show one intense band in the region 260–275 nm ($\log \epsilon = 5.4\text{--}5.8$) which is attributed to the triazole ring (Rao 1961; Khadem *et al* 1963). Table 3 shows the IR spectral data of vicinal triazoles. The most important feature of these spectra is the presence and location of the vicinal triazole ring vibrations and ring breathing bands. The bands around $1160\text{--}1180\text{ cm}^{-1}$, $1220\text{--}1260\text{ cm}^{-1}$ are attributed to vicinal triazole ring vibrations. The peaks around 1130 cm^{-1} , $1050\text{--}1100\text{ cm}^{-1}$, 1000 cm^{-1} and 900 cm^{-1} are assigned to vicinal triazole ring breathing and $C-H$ in-plane deformations. These values are in agreement with the values reported for vicinal triazole ring system (Rao and Venkatraghavan 1964). The absence of a $N-O$ band in triazoles indicates the formation of the triazole ring with the disappearance of the $-OH$ of the oximino group of oximinothiosemicarbazone during the cyclodehydration reaction. The bands around 3450 cm^{-1} and 3300 cm^{-1} are assigned to primary amine $N-H$ and *trans* associated secondary amide $N-H$ stretchings respectively. The band around 1330 cm^{-1} may be assigned to $C=S$ stretching (Wiles *et al* 1967). The bands due to $C=N$ and secondary amide ($C=O$) stretchings are located at their usual positions (Rao 1961).

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Effect of substitution on the catecholate ring on ternary complex stability

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Abstract. The formation constants of the complexes of the type $[\text{CuAL}]$, where $A = 2,2'$ -bipyridyl, 1,10-phenanthroline, 2-(2'-pyridyl)benzimidazole, or 2-(2'-pyridyl)imidazoline and $L =$ a dianion of catechol, tiron, protocatechuic acid, pyrogallol, 1,8-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, dopamine, or adrenaline, have been determined in a dioxan-water (1:1, v/v) medium and $\mu = 0.2 \text{ mol dm}^{-3} \text{ NaClO}_4$ at 30°C , using SCOGS method. The effect of the π acid character of A and substitution on ligand L on the ternary complex stability have been discussed.

Keywords. Ternary complexes; catechol complexes; effect of substitution on ligand.

1. Introduction

The complexes $[\text{MAL}]$, where $A =$ heteroaromatic N-bases, are known to have a statistical stability due to $M \rightarrow A\pi$ interaction (Sigel 1967; Bhattacharya and Chidambaram 1970; Griesser and Sigel 1970). The complex $[\text{MA}]$ shows a discriminating effect towards ligands L , preferring them in the order $\text{O}^--\text{O}^- > \text{O}^--\text{N} > \text{N}-\text{N}$ (Griesser and Sigel 1970; Griesser *et al* 1969, 1973; Bhattacharya *et al* 1982a). The effect is maximum in case of Cu(II) complexes and $\Delta \log K$ is positive in $[\text{CuA O}^--\text{O}^-]$ complexes. Larger positive values of $\Delta \log K$ have been observed in $[\text{CuAL}]$ complexes where L is the aromatic ligand with O^--O^- co-ordinating sites (Griesser *et al* 1971, 1973; McCormick *et al* 1972).

The stabilization of the ternary complex depends on the π acid character of the base A . The greater the $M \rightarrow A \pi$ interaction, the stabler is the ternary complex (Bhattacharya *et al* 1982b). It has also been shown that substitution on the ligand L affects the stability of the ternary complex. It was observed (McCormick *et al* 1972; Huber *et al* 1971) that the substitution of an electron withdrawing group on the secondary ligand L in $[\text{CuAL}]$ complexes destabilizes the ternary complex, and of an electron-releasing group increases the stability of the ternary complex. It has recently been observed by Bhattacharya and Patel (1984a) that in $[\text{CuAL}]$ complexes where $L =$ salicylaldehyde and its derivatives, $\Delta \log K$ becomes less positive with the increasing electron-withdrawing tendency of the substituted groups. In order to investigate this further, complexes $[\text{MAL}]$ have been studied where $M = \text{Cu(II)}$, $A = 2,2'$ -bipyridyl (A^1), 1,10-phenanthroline (A^2), 2-(2'-pyridyl)benzimidazole (A^3), 2-(2'-pyridyl)imidazoline (A^4), and $L =$ the dianion of catechol (L^1), tiron (L^2),

dihydroxynaphthalene (L^6), dopamine (L^7), or adrenaline (L^8). Some of the systems have already been studied (Griesser and Sigel 1970; McCormick *et al* 1972; Huber *et al* 1971) in aqueous media but the formation constants have again been determined in 50% dioxan-water (1:1, v/v) media for comparison under identical experimental conditions.

2. Experimental

All reagents used were of AR grade except 2-(2'-pyridyl)benzimidazole and 2-(2'-pyridyl)imidazoline, which were synthesised (Frieser and Walter 1954). The pH was measured to an accuracy of ± 0.01 . Necessary pH corrections for the dioxan-water medium were made (Haas and Van Uitert 1953).

The proton-ligand, binary metal-ligand and ternary complex formation constants were determined in dioxan-water (1:1, v/v) medium and $\mu = 0.2 \text{ mol dm}^{-3} \text{ NaClO}_4$ at 30°C by using scogs computer technique (Sayce 1968, 1971; Sayce and Sharma 1972). In every case, the titration was repeated for two different concentrations and similar values were obtained as shown in tables 1 and 2.

The formation constants of proton-ligand entities LH , LH_2 and those of the binary complexes $[CuL]$ and $[CuL_2]$ were first obtained. The formation constants of $[CuA]$ and $[CuA_2]$ were determined as done earlier (Bhattacharya and Gopalakrishnan 1982). These values were used as fixed parameters in the refinement of the ternary complex formation constants, $\log K_{CuAL}^{Cu}$. The species present in the solution were considered to

Table 1. Proton-ligand and binary complex stability constants.

Ligand ^a	$\log K_1^H$	$\log K_2^H$	$\log K_3^H$	$\log K_{CuL/A}^{Cu}$	$\log K_{CuL_2/A_2}^{CuL/A}$
L^1	12.97 (0.00)	8.97 (0.05)	—	12.80 (0.03)	10.00 (0.01)
L^2	12.98 (0.01)	8.07 (0.02)	—	14.41 (0.01)	12.91 (0.02)
L^3	12.38 (0.03)	9.61 (0.00)	5.85 (0.02)	15.56 (0.10)	10.82 (0.20)
L^4	12.54 (0.10)	9.79 (0.10)	—	15.41 (0.10)	13.33 (0.30)
L^5	10.04 (0.06)	8.35 (0.00)	—	10.57 (0.04)	9.09 (0.06)
L^6	12.78 (0.01)	9.62 (0.01)	—	14.55 (0.06)	11.92 (0.10)
L^7	11.40 (0.10)	10.76 (0.08)	8.83 (0.10)	14.00 (0.04)	11.66 (0.07)
L^8	13.11 (0.10)	9.86 (0.02)	8.75 (0.10)	14.66 (0.20)	12.22 (0.02)
A^1	3.70 (0.04)	—	—	7.00	4.15 (0.15)
A^2	4.40 (0.03)	—	—	8.82	5.46 (0.12)

Values in dioxan-water (1:1, v/v) and $\mu = 0.2 \text{ M NaClO}_4$ at 30°C , with standard deviation $\sigma\beta$ in parentheses: ^a see text for ligand description.

Table 2. Stability constants for ternary complexes of Cu(II).

Ligands ^b	$\log K_{\text{CuAL}}^{\text{CuA}^a}$							
	A ¹		A ²		A ³		A ⁴	
	log K	$\Delta \log K$	log K	$\Delta \log K$	log K	$\Delta \log K$	log K	$\Delta \log K$
L ¹	13.60 (0.08)	+0.80	13.48 (0.07)	+0.68	14.12 (0.09)	+1.32	12.33 (0.01)	-0.47
L ²	14.39 (0.01)	-0.02	14.25 (0.01)	-0.16	14.50 (0.02)	+0.09	12.80 (0.05)	-1.61
L ³	15.04 (0.10)	-0.52	15.24 (0.10)	-0.32	15.71 (0.10)	+0.15	14.40 (0.09)	-1.16
L ⁴	15.04 (0.10)	-0.37	14.77 (0.10)	-0.79	15.74 (0.06)	+0.18	14.27 (0.06)	-1.29
L ⁵	9.05 (0.00)	-1.52	8.93 (0.03)	-1.64	10.64 (0.03)	+0.07	8.91 (0.03)	-1.66
L ⁶	14.92 (0.01)	+0.37	14.71 (0.01)	+0.16	15.14 (0.02)	+0.59	13.79 (0.02)	-0.76
L ⁷	13.94 (0.10)	+0.06	13.47 (0.02)	-0.53	14.75 (0.04)	+0.75	13.29 (0.04)	-0.71
L ⁸	15.27 (0.10)	+0.61	15.22 (0.10)	+0.56	16.58 (0.05)	+1.92	14.38 (0.05)	-0.28

Values in dioxan-water (1:1, v/v) and $\mu = 0.2 \text{ M NaClO}_4$ at 30°C, with standard deviation $\sigma\beta$ in parentheses;

^a using computer method; ^b see text for ligand description.

be AH, A, LH₂, LH, [CuA], [CuA₂], [CuL], [CuL₂] and [CuAL]. The preliminary value of $\log K_{\text{CuAL}}^{\text{CuA}}$ supplied to the computer, was obtained by considering the reaction to be of the type $[\text{CuA}] + \text{L} \rightleftharpoons [\text{CuAL}]$ (Bhattacharya *et al* 1982b).

Spectra were recorded (Carl Zeiss Specord UV visible spectrophotometer) using dioxan-water (1:1, v/v) as solvent. The spectra of Cu(II) + A + L mixed in 1:1:1 mole ratio were recorded at pH 5.8, where mixed ligand complex formation is maximum. The observed spectral bands in the visible range are presented in table 3.

3. Results and discussion

From the plot of the concentration of the species against pH, it is observed that in the lower pH range (pH 1.8–3.0) Cu(II) and [CuA] are the major species and in the higher pH range (pH 4.0–7.0) the species [CuA] and [CuAL] predominate. Formation of [CuA₂], [CuL] and [CuL₂] is low. In all cases upto 98% of the mixed-ligand complexes are formed and the sum of [CuAL] and [CuA] is almost 100%. This shows that these complexes are formed in steps $\text{Cu} + \text{A} \rightleftharpoons [\text{CuA}]$ and $[\text{CuA}] + \text{L} \rightleftharpoons [\text{CuAL}]$, equilibrium constants for which are given in tables 1 and 2.

The formation constants show that in the complexes [CuAL] where A = A¹, A² or A³ and L = L¹, L⁶ or L⁸, $\Delta \log K$ ($\log K_{\text{CuAL}}^{\text{CuA}} - \log K_{\text{CuL}}^{\text{CuA}}$) is positive.

In cases where A = A⁴, $\Delta \log K$ is negative for all the mixed ligand complexes. In cases where L = L², L³, L⁴, L⁵ or L⁷, $\Delta \log K$ is negative except where A = 2-(2'-

Table 3. Electronic spectra of binary and ternary complexes.

Compound ^a	λ max in cm^{-1}
$[\text{CuA}_2^1]$	13 500 (2.79)
$[\text{CuA}_2^2]$	13 500 (2.75)
$[\text{CuL}_2^1]$	22 120 (1.59), 14 600 (1.19)
$[\text{CuL}_2^2]$	22 500 (1.36), 13 250 (1.16)
$[\text{CuL}_2^3]$	25 000 (sh) (2.27), 14 390 (1.44)
$[\text{CuL}_2^4]$	24 700 (1.89), 14 490 (1.58)
$[\text{CuL}_2^5]$	21 000 (sh) (1.95), 13 160 (1.31)
$[\text{CuL}_2^7]$	17 000 (1.79), 12 900 (0.95)
$[\text{CuL}_2^8]$	21 500 (2.16), 12 660 (0.65)
$[\text{CuA}^1\text{L}^1]$	22 000 (1.85), 13 790 (1.11)
$[\text{CuA}^1\text{L}^2]$	22 500 (1.90), 14 390 (1.32)
$[\text{CuA}^1\text{L}^3]$	24 000 (2.08), 15 030 (1.20)
$[\text{CuA}^1\text{L}^4]$	23 250 (2.49), 15 000 (1.11)
$[\text{CuA}^1\text{L}^6]$	21 000 (2.02), 13 160 (1.30)
$[\text{CuA}^1\text{L}^7]$	22 000 (2.04), 16 000 (2.04)
$[\text{CuA}^1\text{L}^8]$	22 500 (1.95), 14 290 (1.07)

Values in dioxan-water (1:1, v/v) medium; ^a see text for ligand descriptions; Values of $\log \epsilon$ (epsilon in units of $\text{M}^{-1} \text{cm}^{-1}$) are given in parentheses.

For all complexes the order of formation constants is $[\text{CuA}^3\text{L}] > [\text{CuA}^1\text{L}] \approx [\text{CuA}^2\text{L}] > [\text{CuA}^4\text{L}]$, as expected from the increasing order of $\text{Cu} \rightarrow \text{A}$ π interaction (Bhattacharya *et al* 1982a). As $\text{Cu} \rightarrow \text{A}$, π interaction goes on increasing, $\Delta \log K$ becomes more positive in $[\text{CuAL}]$ where $\text{L} = \text{L}^1, \text{L}^6$ or L^8 and less negative in cases, where $\text{L} = \text{L}^2, \text{L}^3, \text{L}^4, \text{L}^5$, or L^7 .

The positive $\Delta \log K$ in the complexes $[\text{CuAL}]$, where $\text{L} = \text{L}^1, \text{L}^6$ or L^8 , is as expected in cases of $\text{O}^- - \text{O}^-$ coordinating ligands (Griesser and Sigel 1970; Griesser *et al* 1973; Bhattacharya *et al* 1982a). This has been explained as due to the increasing class A character of Cu(II) in $[\text{CuA}]$, with consequent decrease of repulsion between the metal $d\pi$ electrons and the lone pair of electrons over the ligand atom in the ternary complex (Bhattacharya *et al* 1982a). The effect is maximum in case of $\text{O}^- - \text{O}^-$ ligands with lone pairs of electrons over both O^- (Griesser and Sigel 1970; Bhattacharya *et al* 1982a). The effect is larger when the two O^- are over the aromatic ring (McCormick *et al* 1972; Griesser and Sigel 1971, 1973).

With the substitution of the aromatic ring H by electron withdrawing groups, the electron density over O^- is reduced. This destabilizes the ternary complex and makes $\Delta \log K$ less positive. An electron releasing group increases the electron density over O^- and stabilizes the ternary complex resulting in more positive $\Delta \log K$.

In cases, where $\text{L} =$ the dianion of 2,3-dihydroxynaphthalene (L^6), $\Delta \log K$ is less positive than in cases where $\text{L} =$ catecholate (L^1). This can be explained by considering that the lone pair electrons on the two O^- of 2,3-dihydroxynaphthalene get delocalized over two rings and hence, the effective electron density on the O^- is less in case of L^6 than in case of catecholate. Thus, the additional phenyl ring acts as an electron

the ligand co-ordinates through two O^- . This is because the two O^- are on different benzene rings and hence the effective negative charge on the two O^- is less, which leads to negative $\Delta \log K$.

It is also seen that in $[CuA \text{ tiron}]$, $[CuA \text{ protocatechuate}]$ or $[CuA \text{ pyrogallolate}]$ complexes, $\Delta \log K$ values are negative or less positive than in case of $[CuA \text{ catecholate}]$. This is expected because the substituted sulphonate, carboxylate and hydroxy groups on the rings of ligands L^2 , L^3 and L^4 , respectively, reduce the electron density on the ring. Thus, the negative charge over two O^- is less in these ligands than in the case of unsubstituted catecholate, and $\Delta \log K$ is less positive.

In cases where $L = \text{dopamine } (L^7)$ or $\text{adrenaline } (L^8)$ also, co-ordination is from the phenolate O^- . This has been confirmed by observing visible spectral bands. There is difference in the $d-d$ spectral band positions of $[CuA^1L^7]$ ($16,000 \text{ cm}^{-1}$), $[CuA^1L^8]$ ($14,290 \text{ cm}^{-1}$) and $[CuA^1L^1]$ ($13,790 \text{ cm}^{-1}$) because of the substitution effect in the first two cases. But a band at $\sim 22,000 \text{ cm}^{-1}$ is seen in all these complexes (table 3), which is characteristic of the $L \rightarrow M$ charge transfer in catecholate complexes (Mainer and Rajan 1978). This shows that the amine group is not involved in co-ordination. The proton association constant of the amine in these ligands is higher and the proton does not dissociate till pH 7.5. Hence, in the pH range 3.0–6.0, where L co-ordinates with $[CuA]$, it can be considered to be in the monoprotonated form LH , the amine proton remaining undissociated. The formation constants show that in the case of $[CuAL^8H]$, $\Delta \log K$ is less positive than in the case of $[CuAL^1]$ and in the case of $[CuAL^7H]$, $\Delta \log K$ is negative when $A = A^1, A^2$, or A^4 . Decrease in the $\Delta \log K$ values in the case of catecholamines is because the protonated amine group withdraws electron density from the ring; hence, the ternary complex is not stabilized to the same extent as $[CuAL^1]$. The electron withdrawing effect is less in adrenaline (L^8) than in dopamine (L^7), probably because of the additional methyl group.

Thus, the present study shows the effect of substituted groups, not directly co-ordinated to the metal ion, on ternary complex stability. Catechol and its derivatives, like catecholamines, are of biochemical importance and their degradation is brought about by the metalloenzymes co-ordinating with the two phenolate O^- of the catechol part, which is then oxidized to quinone. The present study also shows that the substituted amine group in catecholamines may make them less susceptible to co-ordination with metalloenzymes involving imidazole type of ligands (Bhattacharya and Patel 1984b).

3.1 Visible spectra

It is normally expected that in a mixed-ligand complex $[MAL]$, the ligand field created by the two ligands is the average of the ligand fields in the binary complexes $[MA_2]$ and $[ML_2]$ (Kida 1961). This is true in complexes $[CuAL]$, where L co-ordinates through N-N or O^- -N (Bhattacharya *et al* 1982a). However, in the complex $[CuAL]$ studied in the present paper, where L co-ordinates through two O^- , the $d-d$ transition band in $[CuAL]$ is at a higher energy level than in $[CuA_2]$ or $[CuL_2]$. This shows that the $M \rightarrow \text{bipy } \pi$ interaction stabilizes the $L \rightarrow M \sigma$ interaction (where L co-ordinates through two O^-). Conversely, the $L \rightarrow M \sigma$ interaction increases the $M \rightarrow \text{bipy } \pi$ interaction. Thus the two ligands mutually stabilize each other. Consequently, ligand A and L create a stronger field in $[CuAL]$ than in $[CuA_2]$ or $[CuL_2]$.

Acknowledgement

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A high-spin iodo-arsine ruthenium(III) complex

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Abstract. A metathetical reaction conducted between $\text{RuCl}_3(\text{AsPh}_3)_2(\text{MeOH})$ and a large excess of NH_4I afforded a high-spin pentacoordinate complex, $\text{RuI}_3(\text{AsPh}_3)_2$ (high-spin/paramagnetic/triphenylarsine/iodide/ruthenium(III) complex).

Keywords.

1. Introduction

The synthesis of several ruthenium(II) and (III) complexes involving monotertiary phosphines and arsines under a variety of reaction conditions were reported from our laboratory over the last few years (Taqui Khan and Veera Reddy 1981, 1982, 1983). As part of a general synthetic programme and in an attempt to prepare the iodo analogue of Wilkinson's complex, $\text{RuCl}_3(\text{AsPh}_3)_2(\text{MeOH})$ (Stephenson and Wilkinson 1966), we report here the synthesis and characterisation of a new high-spin complex of the composition $\text{RuI}_3(\text{AsPh}_3)_2$.

2. Experimental

Preparation of the complex: The complex $\text{RuCl}_3(\text{AsPh}_3)_2(\text{MeOH})$ (0.20 gm, 0.23 mM) was dissolved in benzene and refluxed with a methanolic solution of NH_4I (0.34 gm, 2.3 mM) for three hours in an atmosphere of nitrogen. The solution was cooled to room temperature. The dark green powder obtained was filtered and washed with 1:1 methanol-water till it gave no test for Cl^- or I^- and finally washed with methanol. The product was recrystallised from dichloromethane-*n*-hexane solvent system and dried *in vacuo*. Yield: 0.20 gm (80%). Analysis (%), Found: C 38.6; H 2.8; I 33.3. Calcd: C 39.5; H 2.7; I 34.8. The complex decomposes above 182°C.

The molecular weight of the complex was measured in chloroform as reported earlier (Taqui Khan and Veera Reddy 1983) and was found to be 960 as against the calculated value of 1094. Magnetic susceptibility of the complex was measured with the solid sample on a Faraday balance at room temperature and the μ_{eff} was found to be 5.12 B.M. The conductivity of the complex in Dimethylacetamide (DMA) indicates that it is a non-electrolyte ($\lambda_{\infty} = 21.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$).

3. Discussion

The elemental analysis, in conjunction with the conductivity value of the complex, confirms the presence of three iodides in the coordination sphere of the metal ion. Molecular weight measurements on this complex suggest that it is a monomeric pentacoordinate complex. The far-infrared spectrum tentatively supports the formulation of this complex as axially symmetric with three iodides in the trigonal base and the two arsines in the axial positions. Thus a single intense band at 476 cm^{-1} due to ν (Ru-As) and two weak bands at 188 and 208 cm^{-1} due to ν (Ru-I) are in conformity with the proposed structure for the complex. This is also in accord with the observations made earlier on similar complexes, RuCl_3L_2 ($\text{L} = \text{AsPh}_3$ Manoharan *et al* 1973, $\text{AsTol}_3^{\text{para}}$ Taqui Khan and Veera Reddy 1983). The assignment of trigonal bipyramidal geometry is rare for a d^5 configuration, since such geometries occur mostly in d^0 , d^8 and d^{10} configurations. However, some five coordinate metal complexes having trigonal bipyramidal structure with d^5 configuration have been reported in the last decade (Manoharan *et al* 1973; Ruiz-Ramirez *et al* 1973).

The complex shows paramagnetism corresponding to a spin-free d^5 configuration ($\mu_{\text{eff}} = 5.12\text{ B.M.}$). The magnetic moment observed is slightly less than that expected for five unpaired electrons ($\mu_{\text{eff}} = 5.92\text{ B.M.}$) and this lowering may be expected due to the strong-field interaction caused by the coordination of triphenylarsine ligands. Iodide is a weak-field ligand lying to the extreme left of the spectrochemical series and thus favouring the formation of high-spin complexes. Despite the strong-field nature of triphenylarsine, which is a good π -acid, the larger size of iodide makes it difficult for the arsine groups to come close enough to the metal ion, and probably forces the arsine ligands to lie at much longer axial distances than expected from the covalent radii. This is a unique observation because $4d$ and $5d$ transition elements form spin-paired complexes even with weak-field ligands. Since iodo complexes are very unstable, not much is known about the behaviour of $4d$ or $5d$ metal ions in the presence of iodide groups.

On the basis of the magnetic moment of the complex and assuming the complex to be in trigonal bipyramidal (D_{3h}) geometry with spin-free d^5 configuration, the ordering of one-electron levels may be written as: $e''(xz, yz) < a'_1(z^2) < e'(x^2 - y^2, xy)$. The ground state configuration, $(e'')^2 (a'_1)^1 (e')^2$ leads to the ground state energy level A'_1 (Muetterties and Schunn 1966). The electronic transitions based on excited state configurations (quartets and doublets) will be all spin-forbidden. The electronic transitions observed at 800 nm ($\epsilon = 510$), 660 nm ($\epsilon = 864$), 380 nm ($\epsilon = 3014$) and 330 nm ($\epsilon = 4360$) may be, therefore, all charge-transfer bands or the low-intensity $d-d$ bands overlapped with charge-transfer bands.

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Polarographic study of the irreversible system of zinc(II) with L-histidine/1,2-diaminopropane

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Abstract. Binary complexes of zinc(II) with L-histidine/1,2-diaminopropane have been studied by using amalgam polarography. The characteristic of the composite polarograms show the irreversible nature of the electrode reaction process. The kinetic parameters such as standard rate constant, k_s , and transfer coefficient α , have been determined by Randles' method. Standard rate constants are of the order of $10^{-5} \text{ cm sec}^{-1}$. There is evidence for the presence of $\text{Zn}(\text{histidine})_3$ species. Stability constants have also been determined.

Keywords. Zinc; L-histidine; 1,2-diaminopropane; standard rate constant; transfer coefficient; stability constant.

1. Introduction

Studies on the complexes of cadmium (Islam and Bhat 1981; Ramaiah *et al* 1982; Islam *et al* 1983) with different amino acids and diamines in our laboratory have been continued along with those of zinc(II), using L-histidine and 1,2-diaminopropane as ligands, by polarographic methods. The reduction of binary complexes of Zn(II) with L-histidine/1,2-diaminopropane at the dropping mercury electrode (DME) was found to be irreversible. Hence, amalgam polarography was used to study them and their stability constants were determined. In the presence of both the ligands, it was not possible to determine the satisfactory reversible potentials (or formal potentials). This paper deals with the studies on the irreversible nature of the electrode reaction process, determination of the kinetic parameters and the stability constants of the binary complexes of Zn(II) with L-histidine (his) and 1,2-diaminopropane (pn).

2. Experimental

A manual set-up of the polarograph, with a dropping mercury electrode in connection with a saturated calomel electrode (SCE) as the reference electrode, was used for obtaining current-potential curves. Measurements were carried out in the deaerated solution at $30 \pm 0.1^\circ\text{C}$ in the presence of a supporting electrolyte, KCl. The ionic strength was maintained at 0.5 M.

The capillary characteristics were: $m = 1.50 \text{ mg sec}^{-1}$ and $t = 3.85 \text{ sec}$ (open circuit). Zinc sulphate (BDH, Analar) solution was standardised (Vogel 1968) by the oxinate

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method. L-histidine (Puriss, Fluka, AG) and 1,2-diaminopropane (E Merck) were used without further purification. 1,2-diaminopropane solution was standardised with standard hydrochloric acid using methyl red as indicator. 0.006 % gelatin was used to suppress the pronounced maximum. Double distilled water was used for the preparation of the solution.

The dropping amalgam electrode was prepared according to Sundaresan *et al* (1967). A Radiometer pH meter was used for measuring the pH of the solution.

3. Results and discussion

3.1 Zinc-L-histidine system

A well-defined wave was obtained for zinc(II) with the half-wave potential at -1.003 V vs SCE. The composite polarograms of the solution were taken at 0.3 mM concentration of zinc(II) at different pL ($= -\log[\text{his}]$) values. It is found from the nature of the curves that the irreversibility increases with the increase of concentration of L-histidine. A few composite polarograms are presented in figure 1. The reversible potentials, E_r , were calculated from zero current potential by using Randles' (Randles 1962) method. The reversible potentials were used to calculate the formal potentials, E_f^0 , from the Nernst equation substituting the cathodic and anodic diffusion currents for the concentrations of oxidant and reductant, respectively. E_f^0 values at different pL values are tabulated in table 1.

Formal potentials were used for the calculation of over potential, η . The standard rate constant, k_s , and transfer coefficient, α , were evaluated from the cathodic waves using the method described by Chandrasekharan *et al* (1968). The values were obtained from a plot of $\log \{h/[1 + \exp(nF/RT)\eta]\}$ vs η (eqn (1)).

$$\log h/[1 + \exp(nF/RT)\eta] = \log (3/7D)^{1/2} k_s - \alpha nF/(2.303 RT)\eta, \quad (1)$$

k_s and α values are presented in table 1.

It is observed that the standard rate constants are of the order of 10^{-5} cm sec $^{-1}$ which shows the irreversible nature of the electrode reaction. Using the values of k_s and α , the current, i at different potentials were calculated with the help of (2) (Chandrasekharan *et al* 1968) and plotted to obtain

$$[(i_d) - i]/i = (1.13/k_s)(D/t)^{1/2} \exp(\alpha nF/RT)\eta + \exp(nF/RT)\eta \quad (2)$$

current-potential curves. These curves fitted well with the experimental curves. As the plot of E_f^0 vs pL gave a curve indicating the presence of a mixture of complexes, DeFord and Hume's (1951) method was applied for the determination of stability constants.

The $F_0(L)$ function for the second and third species can be written as

$$F_0(L) = 1 + \beta_2(L)^2 + \beta_3(L)^3 \quad (3)$$

$F_0(L)$ can be calculated from the measurable quantities as

$$F_0(L) = \text{antilog} \left[\left\{ 0.4343 \frac{nF}{RT} \Delta E_f^0 \right\} + \log \frac{(i_d)_s}{(i_d)_c} \right] \quad (4)$$

where the symbols have their usual significance. $F_0(L)$ values are given in table 1. The

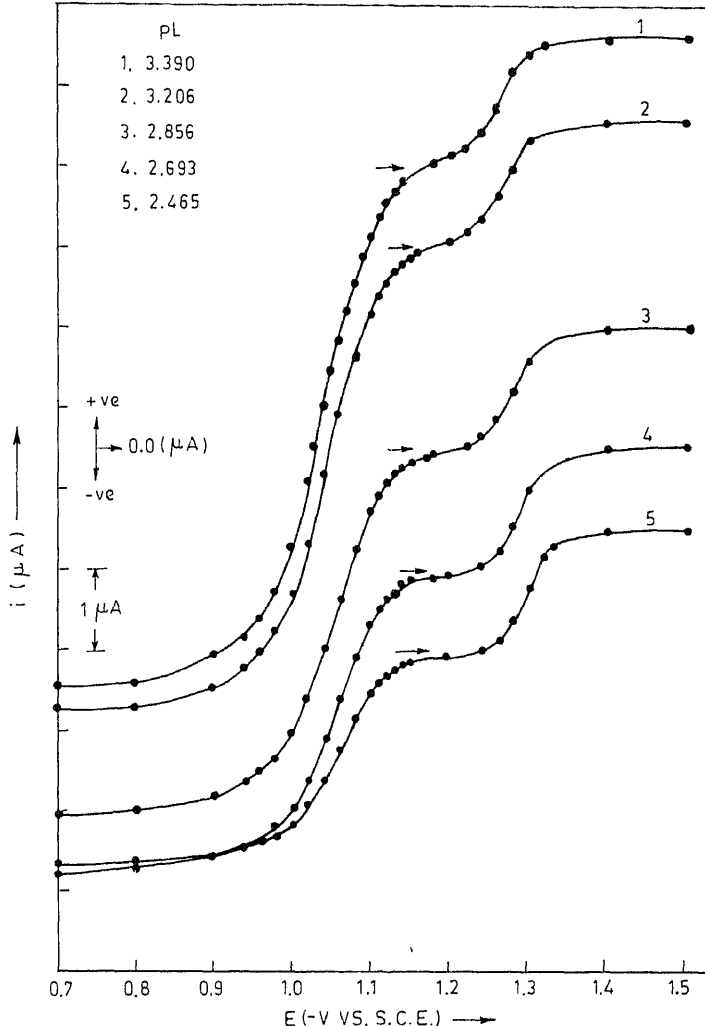


Figure 1. Composite polarograms; zinc-L-histidine system.

$\log \beta_2 = 11.75$ and $\log \beta_3 = 14.09$. The $\log \beta_2$ value agrees well with the literature value (Leberman and Rabin 1959). The calculated value of $\log \beta_1 = 6.55$.

An important feature of this investigation is the presence of $Zn(his)_3$ as one of the complex species; this has not been reported earlier. Histidine is a potential terdentate ligand (Beech 1969), coordination being possible from the imidazole nitrogen atom, the amino group and the carboxyl group. Thus histidine may act as unidentate, bidentate or terdentate ligand. Williams (1970) and Perrin and Sharma (1967) have suggested that zinc coordinates tetrahedrally in the $Zn(his)_2$ complex and the two carboxylic groups are only loosely bound. Chakravarty and Cotton (1963) have also found in their x-ray crystallographic studies of the zinc-histidine complex that coordination occurs through the tertiary imidazole nitrogen and α -amino nitrogen. The carboxyl oxygens are at

no bond formation possible. Comparing the log K values for copper and zinc or histidine and histamine complexes, Perrin and Sharma (1967) have concluded that histidine is bidentate in nature rather than terdentate in zinc-histidine complex. On the basis of this assumption it may be possible to form a octahedral $Zn(his)_3$ species at higher concentration of histidine.

3.2 Zinc-1,2-diaminopropane system

Under same experimental conditions as described in the previous section, the composite polarograms of zinc (0.3 mM) in the presence of 1,2-diaminopropane of different concentrations were obtained. The characteristics of the composite polarograms show the irreversible nature of the electrode reaction. The reversible potentials and the formal potentials were calculated by using the same method as in the case of zinc-histidine system. k_s , α and $F_0(L)$ values are given in table 2, $\log \beta_2 = 10.23$ and

Table 1. Zinc-L-histidine system.

pL	α	$-\log k_s$	E_f^0 ($-V$ vs SCE)	$F_0 \times 10^{-5}$	$F_1 \times 10^{-8}$	$F_2 \times 10^{-11}$	$F_3 \times 10^{-14}$
5.000	—	—	1.054	0.0005	—	—	—
4.598	—	—	1.078	0.003	—	—	—
4.215	—	—	1.104	0.026	—	—	—
3.807	—	—	1.126	0.120	—	—	—
3.390	—	—	1.154	1.123	—	—	—
3.206	0.55	4.58	1.166	2.648	—	—	—
3.066	0.56	4.64	1.174	4.741	5.570	6.540	1.045
2.856	0.65	4.99	1.188	14.070	10.196	7.388	1.250
2.693	0.69	4.99	1.200	35.825	17.544	8.591	1.440
2.465	0.68	4.79	1.216	121.110	34.932	10.075	1.270
2.310	0.68	4.70	1.227	274.898	56.136	11.463	1.186

$\log \beta_2 = 11.75$; $\log \beta_3 = 14.09$

$$\text{Zn} = 0.3 \text{ mM}; \mu = 0.5 \text{ M (KCl)}; (E_{1/2})_S = -1.003 \text{ V (vs SCE)}.$$

Table 2. Zinc-1,2-diaminopropane system.

pL	α	$-\log k_s$	E_f^0 (-V vs SCE)	$F_0 \times 10^{-4}$	$F_1 \times 10^{-7}$	$F_2 \times 10^{-10}$	$F_3 \times 10^{-13}$
4.040	—	—	1.070	0.016	—	—	—
3.166	—	—	1.236	1.029	—	—	—
3.054	0.57	4.28	1.131	1.800	—	—	—
2.941	—	—	1.135	2.540	2.217	1.934	0.200
2.817	0.62	4.46	1.144	4.762	3.124	2.050	0.229
2.718	—	—	1.153	9.416	4.919	2.570	0.454
2.558	0.67	4.62	1.162	19.199	6.938	2.507	0.291
2.362	0.68	4.54	1.177	61.988	14.267	3.283	0.364
2.228	—	—	1.187	132.337	22.373	3.782	0.354
2.188	0.65	4.44	1.190	162.745	25.092	3.869	0.334

$\log \beta_2 = 10.23$; $\log \beta_3 = 12.54$

$\log \beta_3 = 12.54$, obtained graphically, agree well with literature values (Carlson *et al* 1945). Calculated value of $\log \beta_1 = 6.21$.

The values ($\log \beta_{10} = 12.60$ and $\log \beta_{20} = 15.00$) reported by Gupta *et al* (1980) appear to be high compared to those obtained in the present study and others (Sillen and Martell 1971). The high values may be due to the fact that Gelling's formulation (1962, 1963) is not applicable for an irreversible system. Tanaka and Tamamushi (1963) have successfully used Gelling's formulation for studying systems having $k_s > 10^{-3} \text{ cm sec}^{-1}$ only.

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Studies on some organotin(IV) complexes of azomethines derived from sulphad rugs

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Abstract. Equimolar reactions of Bu_2SnO and Ph_2SnO with azomethines derived by the condensation of salicylaldehyde with some well known sulphad rugs *viz.* sulphathiazole, sulphaphenazole, sulphadiazine, sulphaguanidine and 2-(*p*-aminobenzene sulphonamido)-4,5-dimethyl oxazole yield a new series of organotin(IV) complexes. The infrared and proton magnetic resonance spectral studies indicate coordination of phenolic oxygen and azomethine and secondary amino nitrogens providing a five coordinated environment at the tin atom.

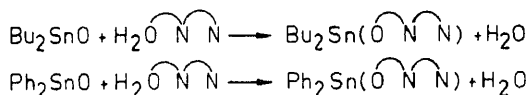
Keywords. Organotin(IV) complexes; azomethines; sulphad rugs; IR spectra; proton magnetic resonance spectra.

1. Introduction

In earlier publications from these laboratories, the syntheses of a variety of tin(II) and tin(IV) derivatives with different types of Schiff bases have been reported (Varshney and Tandon 1984a,b,c; Saxena *et al* 1982, 1984; Saxena and Tandon 1983). However, organotin(IV) complexes of azomethines derived from sulphad rugs have not been studied so far. In this paper, we report the synthesis and characterization of organotin(IV) derivatives with ligands derived by the condensation of salicylaldehyde with sulphathiazole, sulphaphenazole, sulphadiazine, sulphaguanidine and 2-(*p*-aminobenzene sulphonamido)-4,5-dimethyloxazole.

2. Discussion

The reactions of dibutyltin oxide or diphenyltin oxide with the above mentioned azomethines, in benzene in 1:1 molar ratio, take place as follows:



All the newly synthesized complexes are coloured solids, insoluble in common organic solvents but soluble in DMSO and DMF.

The molar conductance measurements in anhydrous DMF at room temperature (6 to $8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) show that these complexes behave as non-electrolytes; the molecular weight determinations indicate their monomeric nature.

2.1 Infrared spectra

In the IR spectra of complexes, no band in the region $3100\text{--}3450\text{ cm}^{-1}$ assignable to ν_{OH} and ν_{NH} could be observed due to their deprotonation on complex formation with the metal ion. A strong band in the region, $1595\text{--}1620\text{ cm}^{-1}$ may be assigned to $\nu_{\text{C=N}}$, which gets shifted to the lower range as compared to its position in the ligands, due to the coordination of azomethine nitrogen to the tin atom (Saxena *et al* 1982). A medium intensity band in the ligand at $\sim 1280\text{ cm}^{-1}$ due to the $\nu_{\text{C-O}}$ vibrations gets shifted to a higher frequency ($\sim 1300\text{ cm}^{-1}$) range in complexes indicating the participation of phenolic oxygen in coordination (Biradar and Kulkarni 1971). Besides these, several new and sharp to medium intensity bands are observed in the regions $510\text{--}530\text{ cm}^{-1}$ and $440\text{--}380\text{ cm}^{-1}$, due to $\nu_{\text{Sn-O}}$ (Saxena *et al* 1983) and $\nu_{\text{Sn-N}}$ (Kawakami and Okawara 1966) respectively, which are not observed in the spectra of azomethines.

2.2 NMR spectra

In the ^1H NMR spectra of salicylaldehyde sulphadiazine broad signals appear at $\delta 10.26$ and $\delta 12.50$ ppm due to the secondary amino (NH) and hydrogen bonded phenolic protons. These signals disappear in the spectra of tin(IV) complexes indicating the chelation of nitrogen and oxygen to tin. The azomethine proton signal (H-C=N) appearing at $\delta 8.80$ ppm in the ligand is shifted downfield on complexation. The complexes, however, show additional signals at $\delta 0.7\text{--}2.0$ ppm owing to the protons of the butyl group as mentioned in table 1.

Thus on the basis of the above evidences, the following structure can be assigned to these complexes:

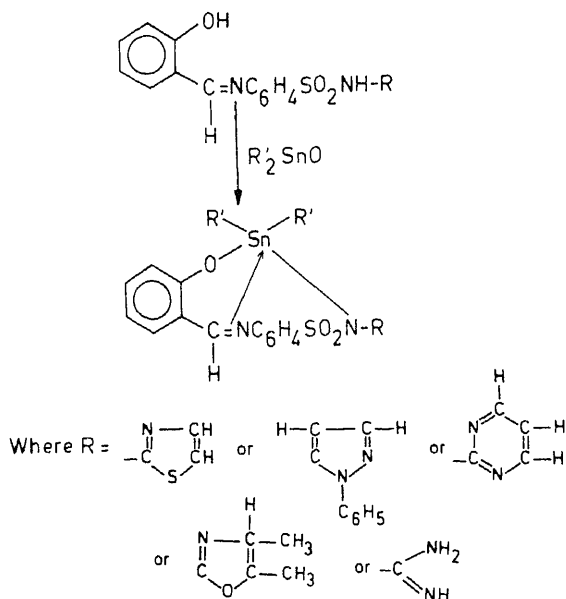
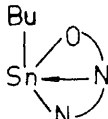
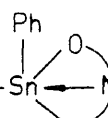


Table 1. ^1H NMR spectral data (δ ppm) of salicylaldehyde sulphadizine and its 1:1 tin(IV) complexes.

Compound	Aromatic protons	OH (H-bonded)	NH (SO ₂ NH)	CH (Azomethine)	Butyl protons
H ₂ ONN-4	6.50–7.80 m	12.50 bs	10.26 s	8.80 s	—
	6.65–7.90 m	—	—	8.9 s	0.70–2.0
	6.60–7.85 m	—	—	8.85 s	—

s = singlet, bs = broad singlet, m = complex multiplet.

3. Experimental

Glass apparatus fitted with quickfit interchangeable joints was used and the reactions were carried out under strictly anhydrous conditions. The fractionations were made on a column packed with Raschig rings and fitted to a ratiohead with a condenser.

3.1 Materials

The azomethines were synthesized by the condensation of salicylaldehyde with the respective sulphadugs in 95% ethanol. The solution was refluxed on a water-bath for 2–3 hours and then allowed to cool at room temperature (Dashora *et al* 1983). The ligands used in these studies are as follows:

- | | |
|---|----------------------|
| (1) Salicylaldehyde sulphathiazole
(C ₁₆ H ₁₃ N ₃ S ₂ O ₃) M.P. 222°C | H ₂ ONN-1 |
| (2) Salicylaldehyde sulphaphenazole
(C ₂₂ H ₁₈ N ₄ SO ₃) M.P. 185°C | H ₂ ONN-2 |
| (3) Salicylaldehyde sulphadiazine
(C ₁₇ H ₁₄ N ₄ SO ₃) M.P. 240°C | H ₂ ONN-3 |
| (4) Salicylaldehyde sulphaguanidine
(C ₁₄ H ₁₄ N ₄ SO ₃) M.P. 230°C | H ₂ ONN-4 |
| (5) 2-(<i>p</i> -amino benzene sulphonamide)-
4,5-dimethyloxazole
(C ₁₈ H ₁₇ N ₃ O ₄ S) M.P. 140°C | H ₂ ONN-5 |

3.2 Analytical methods and physical measurements

The complexes were analysed as reported earlier (Varshney and Tandon 1984b) and

Table 2. Characterisation data of Sn(IV) complexes of azomethines derived from sulphadrigs.

Tin compounds	Azomethines	Compound, colour and state	M.P. °C	Composition found (calcd.) %				Mol. Wt. found (calcd.)
				Sn	N	S		
Bu ₂ SnO	H ₂ ONN-1	Bu ₂ SnC ₁₆ H ₁₁ N ₃ S ₂ O ₃ (yellow powder)	225 s	19.93 (20.12)	6.86 (7.12)	10.24 (10.85)		548 (589.7)
Bu ₂ SnO	H ₂ ONN-2	Bu ₂ SnC ₂₂ H ₁₆ N ₄ SO ₃ (yellow powder)	243 s	17.68 (18.19)	8.26 (8.63)	4.52 (4.93)		627 (648.7)
Bu ₂ SnO	H ₂ ONN-3	Bu ₂ SnC ₁₇ H ₁₂ N ₄ SO ₃ (yellow powder)	210 s	19.62 (20.30)	9.02 (9.57)	5.12 (5.47)		560 (584.7)
Bu ₂ SnO	H ₂ ONN-4	Bu ₂ SnC ₁₄ H ₁₂ N ₄ SO ₃ (dark yellow powder)	215 d	20.98 (21.63)	9.78 (10.20)	5.32 (5.83)		526 (548.7)
Bu ₂ SnO	H ₂ ONN-5	Bu ₂ SnC ₁₈ H ₁₅ N ₃ O ₄ S (dark yellow powder)	160 s	18.96 (19.73)	6.34 (6.98)	4.92 (5.32)		574 (601.7)
Ph ₂ SnO	H ₂ ONN-1	Ph ₂ SnC ₁₆ H ₁₁ N ₃ S ₂ O ₂ (light yellow powder)	200 d	18.68 (19.34)	6.32 (6.84)	10.05 (10.42)		584 (613.7)
Ph ₂ SnO	H ₂ ONN-2	Ph ₂ SnC ₂₂ H ₁₆ N ₄ SO ₃ (light yellow powder)	230 d	16.35 (17.23)	7.84 (8.13)	4.16 (4.64)		664 (688.7)
Ph ₂ SnO	H ₂ ONN-3	Ph ₂ SnC ₁₇ H ₁₂ N ₄ SO ₃ (dark yellow powder)	250 d	18.34 (19.00)	8.32 (8.96)	5.01 (5.12)		601 (624.7)
Ph ₂ SnO	H ₂ ONN-4	Ph ₂ SnC ₁₄ H ₁₂ N ₄ SO ₃ (dark yellow powder)	280 d	19.68 (20.16)	9.12 (9.51)	4.86 (5.43)		566 (588.71)
Ph ₂ SnO	H ₂ ONN-5	Ph ₂ SnC ₁₈ H ₁₅ N ₃ O ₄ S (dark yellow powder)	170 s	17.82 (18.49)	6.03 (6.54)	4.26 (4.98)		613 (641.7)

s = sharp, d = decompose, Calcd. = Calculated.

ance of 10^{-3} M solutions of the complexes was measured at $32 \pm 1^\circ\text{C}$ with conductivity bridge. Infrared spectra were scanned in KBr pellets and NMR spectra DMSO- d_6 or CDCl_3 using TMS as an internal standard at 60 MHz.

3.3 Synthesis of tin(IV) azomethine complexes

Ph_2SnO or Bu_2SnO was dissolved in dry benzene (30–40 ml) and the requisite amount of ligand was added. The contents were refluxed on a fractionating column for about 48 hrs. The water liberated in the reaction was removed azeotropically with benzene. On completion of the reactions, the resulting products were rendered free from the solvent and then washed repeatedly with dry cyclohexane. The products so formed were finally dried *in vacuo* at 60 to 70°C for 2–3 hrs. Their properties and analyses are recorded in table 2.

Acknowledgement

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Synergism in the extraction of uranium (VI) by a mixture of oxine and β -diketones

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Abstract. Extraction of uranium (VI) in presence of a mixture of oxine and β -diketones, viz, benzoyltrifluoroacetone, trifluoroacetylacetone, thenoyltrifluoroacetone and furoyltrifluoroacetone was studied. Extraction was found to be higher than that for oxine or β -diketone alone and the loss of uranium due to precipitation by oxine was eliminated completely. The synergistic species was found to be a mixed chelate and the nature of the species and equilibrium constant were evaluated. A correlation between the two phase stability constants and dissociation constants and partition coefficients of the β -diketones was also established.

Keywords. Synergism; uranium (VI) extraction; oxine; β -diketones.

1. Introduction

Synergism in the extraction of uranium by oxine is of interest since it takes place mainly from chloroform media and the extracted species has been postulated (Vogel 1968) as a self-adduct $[\text{UO}_2(\text{OX})_2 \cdot \text{HOX}]$, unlike the formation of mixed chelates in the case of β -diketones. Extraction of uranium by oxine was very poor from carbon tetrachloride. Investigation of mixed complex formation with other chelates was taken up to study the solubilisation of uranium in the presence of oxine. The formation of adducts by oxine could also lead to synergism of a larger magnitude than in the case of mixed chelates.

2. Experimental

A solution of uranium was prepared from uranyl sulphate (Uranium Extraction Division, BARC). Oxine (BDH, AR), benzoyltrifluoroacetone, trifluoroacetylacetone and furoyltrifluoroacetone (K and K Labs) and thenoyltrifluoroacetone (Koch Light Lab) were used as solutions in carbon tetrachloride (E. Merck GR). The pH of the solution was adjusted with dilute hydrochloric acid or acetic acid-sodium acetate buffer, the concentration of acetic acid was maintained at 0.02 M.

Studies were carried out at $25 \pm 1^\circ\text{C}$ at an ionic strength of 0.5 maintained with sodium chloride. Extraction experiments and the method of estimation of uranium have been described earlier (Malhotra *et al* 1984).

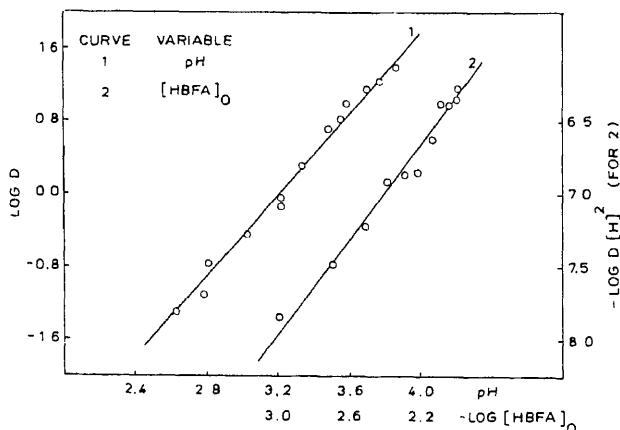
Extraction of uranium (VI) was studied using a mixture of oxine and β -diketones like benzoyltrifluoroacetone (HBFA), furoyltrifluoroacetone (HFTA), thenoyltrifluoroacetone (HTTA) and trifluoroacetylacetone (HTFA) in order to investigate the influence of the terminal group of the β -diketone on synergism.

The concentration of β -diketone in the organic phase was calculated taking into account pK values and partition coefficients (Sekine *et al* 1973). Extraction by individual β -diketones was also investigated. Extraction due to oxine alone could not be studied in detail since extraction was poor at low pH whereas an increase in pH resulted in a gradual loss of metal due to precipitation. The studies were carried out similarly with various β -diketones and hence only the results in the case of HBFA are described.

3.1 Uranium-HBFA-oxine system

Extraction of uranium in the presence of a mixture of HBFA and oxine was found to be considerable and loss of uranium was eliminated completely due to the solubilisation of uranyl oxinate. Extraction was also much higher than that expected for HBFA alone. Such results have not been reported earlier and hence this system has been studied in detail to understand the nature of the complexes.

Experiments were carried out in the pH range of 2.6 to 3.9, keeping the concentrations of HBFA and HOX constant at 0.01 M each. The plot of $\log D$ vs pH resulted in a straight line (figure 1) with a slope of about 2.3. A higher value may be due to the association of oxine with the proton resulting in the formation of H_2OX and hence the extraction mechanism can be postulated as involving two molecules of hydrogen. The plot of $\log D [H^+]^2$ vs $\log [HBFA]_0$ at pH 3.5 to 3.6 and $[HOX]_{tot}$ equal to 0.01 M resulted in a straight line (figure 1) with a slope of about 1.3 indicating the replacement of some of the oxine molecules by HBFA in the formation of the mixed complex.



Experiments were also carried out at a constant concentration of HBFA (0.01 M) and varying amounts of oxine. Since the pH varied during these studies (2.8–3.5) due to the association of protons with oxine, meaningful results could not be obtained from the plot of $\log D$ vs $\log [\text{HOX}]_0$ and hence correction for the association of oxine was made.

The concentration of HOX in the aqueous and organic phase were calculated from the partition coefficient (Leo *et al* 1971) of oxine ($\log P_{\text{HOX}} = 2.06$) and the dissociation constants ($\text{p}K_1 = 5.09$ and $\text{p}K_2 = 9.62$) of oxine (Smith and Martell 1975).

The results indicated the formation of a mixed chelate in which part of HOX was replaced by the β -diketone. To investigate the nature of the extracted species, an analysis of the data based on the formation and extraction of mixed complexes was made (Sudersanan and Sundaram 1978; Pushparaja and Sudersanan 1981).

The distribution ratio, D , for the synergistic reaction can be written as

$$D = \frac{[\text{UO}_2(\text{BFA}) \cdot \text{OX} \cdot \text{HOX}]_0 + [\text{UO}_2(\text{BFA})_2 \text{HOX}]_0}{[\text{UO}_2^{2+}]} \quad (1)$$

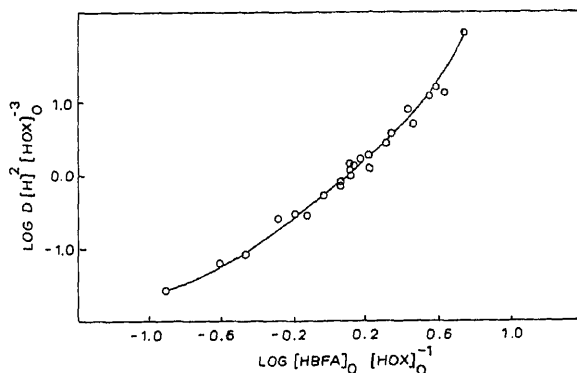
This can be written in terms of the equilibrium constants and on rearranging we get

$$\frac{D[\text{H}^+]^2}{[\text{HOX}]^3} = F_0 = K_{12}[\text{L}] + K_{21}[\text{L}]^2 \quad (2)$$

where $[\text{L}] = [\text{HBFA}]_0/[\text{HOX}]_0$. The function, F_0 , calculated from all the data obtained at varying pH and concentrations of HBFA and HOX fitted in a single curve (figure 2) indicating the validity of the interpretations discussed earlier. The smooth curve was utilised for the calculation of equilibrium constants by a graphical method. The results are summarised in table 1.

3.2 Uranium–HFTA/HTFA/HTTA–oxine systems

Similar studies were made with other fluorinated β -diketones having varying partition coefficients. The plots of $\log \{D[\text{H}^+]^2/[\text{HOX}]_0^3\}$ vs $\log [\text{L}]$, obtained from the data at varying pH and concentrations of the two ligands are presented in figure 3 and were analysed for the nature of the extracted species and their equilibrium constants (table 1). The equilibrium constants for the mixed complexes are quite high, compared



System	β -diketone		$\log K$	$\log P_{mn}\beta_{mn}$	X
	pK	$\log P_{HA}$			
UO ₂ (BFA) ₂ HOX	6.01	2.47	-0.43	16.53	8.48*
UO ₂ (TTA) ₂ HOX	6.28	1.30	0.25	15.41	7.58
UO ₂ (FTA) ₂ HOX	6.18	0.76	0.30	14.18	6.94
UO ₂ (TFA) ₂ HOX	6.09	-0.19	-0.15	11.65	5.90
UO ₂ (BFA)(OX)HOX	6.01	2.47	-0.86	19.30	10.08**
UO ₂ (TTA)(OX)HOX	6.28	1.30	-0.15	19.11	9.63
UO ₂ (FTA)(OX)HOX	6.18	0.76	0.30	18.92	9.31
UO ₂ (TFA)(OX)HOX	6.09	-0.19	0.15	17.73	8.79

$pK_1 = 5.09$; $pK_2 = 9.62$; $\log P_{HA} = 2.06$ for oxine; * $X = \log P_{HA} + pK$; ** $X = 1/2\{\log P_{HA} + pK + (\log P_{HA} + pK_2)_{HOX}\}$.

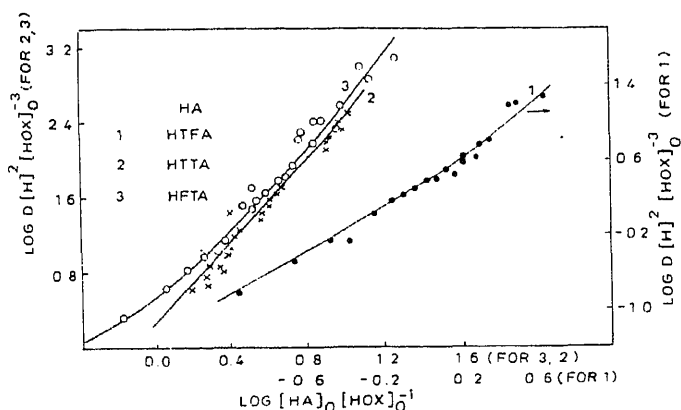


Figure 3. UO₂-HA-Oxine system: plot of $\log F_0$ vs. $\log [L]$

to that for β -diketones alone (which were of the order of 10^{-4} for HTFA and HBFA) since oxine behaves both as a chelating agent and a synergist and hence, the adduct formation with HOX leads to considerable stabilisation of uranium complexes. The values of K_{12} and K_{21} are almost of the same order of magnitude and small differences may be attributed to the relative stabilisation of complexes on the basis of electron distribution and reduced steric hindrance.

In our earlier studies on mixed complexes (Pushparaja and Sudersanan 1981), a correlation was observed between the stability constants of the complexes and the partition coefficients and dissociation constants of the ligands. The applicability of this correlation for the present case was investigated.

The values of $\log P_{21}\beta_{21}$ and $\log P_{12}\beta_{12}$, where P_{mn} and β_{mn} represent the partition coefficient and stability constant of the complex $[UO_2A_m(OX)_{n-1}HOX]$ respectively, were calculated from the experimental values of K_{21} , K_{12} and the pK_a and P_{HA} of the ligands. The values are presented in table 1. A plot of $\log P_{mn}\beta_{mn}$ vs $[\log P_{HA} + pK]$ is presented in figure 4. All the points were on a single line and both the complexes could be interpreted on the basis of this correlation. The slope of the line was also found to be

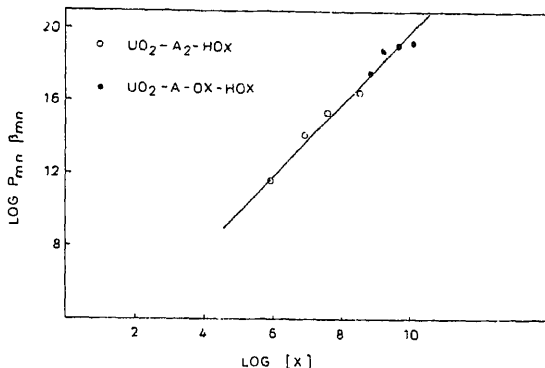


Figure 4. Correlation of equilibrium constants

$$\log P_{mn} \beta_{mn} = 2 [\log P_{HA} + pK] + \text{const.} \quad (3)$$

where the values of $\log P_{HA}$ and pK were calculated as the geometric mean of the participating ligands.

This behaviour indicates the compatibility of the ligands in the inner coordination sphere and also the absence of any steric effect of the ligands on the stabilisation of the complexes. A similar behaviour may also be expected for other β -diketones provided the nature of the ligand does not change so grossly as to introduce other steric effects.

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